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Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators

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LABORATORY AND FIELD EVALUATION OF A METHODOLOGY FOR DETERMINATION OF HYDROGEN CHLORIDE EMISSIONS FROM MUNICIPAL AND HAZARDOUS WASTE INCINERATORS

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16. ABSTRACT

Laboratory and field studies were performed to develop and evaluate a sampling and analytical technique for measuring hydrogen chloride (HCl) from stationary sources. Studies were conducted in three phases: (1) literature search and development of a candidate sampling and analysis protocol, (2) laboratory evaluation and refinement of the protocol, and (3) field evaluation. A modified Method 6 sampling train was selected for sample collection due to its ease of operation, availability, and cost. An acidified water absorbing solution was identified for collecting HCl in the impingers. The acidified water solution was selected to minimize the potential for diatomic chlorine (Cl_2) to interfere with the HCl determination. Ion chromatography was selected as the most suitable technique for the analysis of HCl. The laboratory phase evaluated the HCl collection efficiency of the sampling protocol and the distribution of Cl_2 in the sampling train. A preliminary field test was included in the laboratory phase to indicate any further protocol modifications. A ruggedness test was designed to evaluate the effect of six variables that may be encountered when employing the sampling protocol. A field evaluation was conducted to determine the precision and estimate the accuracy of the sampling and analytical protocol. The candidate method was also employed to determine the bias and precision of two HCl continuous emission monitoring systems.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

Regulations are currently in force to control emissions of HCl from hazardous waste incineration, and the agency is considering regulation of these emissions from municipal waste combustors. In order to support these regulations, work was initiated to develop a method that would be suitable for use as a reference method for measurement of HCl emissions. The development of this reference method will allow the accuracy of continuous emission monitors, which will be used to monitor the HCl emissions, to be determined reliably.

This work was conducted at the request of the Office of Solid Waste.

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ABSTRACT

The U. S. EPA is currently regulating emissions of HCl from hazardous waste incinerators under 40 CFR 264.343 to 4 lbs/hr or an HCl removal efficiency of at least 99%. The EPA is also currently considering regulating HCl emissions from MWC's. Several state and local agencies have already set HCl emission limits for new MWC's and are requiring installation of HCl CEMS's at certain facilities.

Laboratory and field studies were performed to develop and evaluate a sampling and analytical technique for measuring HCl from stationary sources. Studies were conducted in three phases: (1) literature search and development of a candidate sampling and analysis protocol, (2) laboratory evaluation and refinement of the protocol, and (3) field evaluation.

Based on previous studies, a modified Method 6 sampling train with acidified water absorbing solution was selected for collection of HCl. An acidified water solution (0.1 N H_2SO_4) was selected to minimize the potential for Cl_2 to interfere with the HCl determination. Impingers containing an alkaline solution (0.1 N NaOH) and silica gel were added to the train to collect Cl_2 and moisture, respectively, and thus protect the pump and allow determination of percent moisture in the sample gas. Ion chromatography was selected as the most suitable technique for the analysis of HCl.

In a laboratory evaluation, the candidate sampling train was challenged with various combinations of high concentration HCl and Cl_2 cylinder gases to assess the ability of the absorbing solutions to collect and speciate each gas with or without the presence of the other and to examine the effect of flow rate on the adsorption of Cl_2 in the acidic impinger solution. The first acidic impinger showed an HCl collection efficiency of better than 100 percent for all test conditions. Cl_2 separation in the train was 92 percent efficient at a sampling rate of 0.5 lpm and 97 percent efficient at a rate of 2 lpm. The presence of 197 ppm Cl_2 in a 221 ppm HCl gas stream sampled at 2 lpm resulted in an average positive bias in the HCl measurement of 3.4 percent.

A preliminary field evaluation of the protocol was conducted to identify potential sampling problems and analytical interferents and to assess the use of stainless steel versus glass probe tips. The results of the test indicated that both glass and stainless steel probe tips were acceptable for HCl sampling and that a knockout impinger is necessary for use at high moisture (e.g., combustion) sources.

An eight-run, six-variable (low reagent volume, increased impinger pH, longer sampling time, elevated impinger temperature, higher sampling rate, elevated Cl_2 levels, plus a control blank) ruggedness test was used to assess

the effect of deviations from standard sampling conditions. The test results indicated that the method was insensitive to these variables.

A final field evaluation test involving paired midget impinger train sampling concurrent with HCl monitoring at a MWC was used to determine the precision of the HCl sampling and analysis protocol and the bias and precision of two HCl CEMS's. The accuracy of the protocol in terms of the bias was determined by dynamic spiking of the trains using HCl gas cylinders. A series of test runs were also conducted to determine if the amount of CO_2 absorbed by the alkaline impinger reagent would significantly affect the sample volume.

The amount of CO_2 absorbed by the alkaline reagent in both the midget impinger train and a Method 5 train was found to be insignificant. The precision for the HCl sampling and analysis protocol ranged from 0.24 to 0.49 ppm at average flue gas HCl levels of 3.9 to 15.3 ppm. The bias of the protocol ranged from 5.5 to 7.1 percent for HCl cylinder gas concentrations of 9.7 and 34.3 ppm. The bias of two HCl CEMS's relative to the manual protocol ranged from 0.07 to -2.7 ppm at an average flue gas HCl concentration of 3.9 ppm and 0.7 to -5.7 ppm at an average flue gas HCl concentration of 9.9 pm. The precision for the two CEMS's ranged from 0.8 to 0.9 ppm and 1.5 to 2.3 ppm for average flue gas HCl concentrations of 3.9 and 9.9 ppm, respectively. The flue gas HCl concentration trends indicated by the two HCl CEMS's and the manual HCl sampling correlated very well throughout the field test program.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

ANOVA	-- analysis of variance
AREAL	-- Atmospheric Research and Environmental Assessment Laboratory
CEM	-- continuous emission monitoring
CEMS	-- continuous emission monitoring system
CFR	-- Code of Federal Regulations
DAS	-- data acquisition system
DI H_2O	-- deionized water
EMB	-- Emission Measurement Branch
EPA	-- U. S. Environmental Protection Agency
ESP	-- electrostatic precipitator
g	-- gram
GC/ELCD	-- gas chromatograph/electrolytic conductivity detector
GFC	-- gas filter correlation
IC	-- ion chromatography
IEC	-- ion exclusion chromatography
IR	-- infrared
lpm	-- liters per minute
mg	-- milligrams
ml	-- milliliters
mm	-- millimeters
mM	-- millimole
MWC	-- municipal waste combustor
NBS	-- National Bureau of Standards
ppm_{dv}	-- parts per million by volume, dry
ppm_v	-- parts per million by volume
QA/QC	-- quality assurance/quality control
RE	-- relative error
RTI	-- Research Triangle Institute
SCIC	-- single column ion chromatography
SPA	-- spray dryer absorber
SS	-- stainless steel
ug	-- micrograms

SYMBOLS

$CaSO_4$	calcium sulfate (Drierite^R)
Cl^-	chloride ion
Cl_2	diamotic chlorine
CO	carbon monoxide
CO_2	carbon dioxide
$CO_3^=$	carbonate ion

H^+	proton
HCl	hydrogen chloride
HClO	hypochlorous acid
Hg	mercury
H_2O	water
H_2SO_4	sulfuric acid
N_2	nitrogen
NaOH	sodium hydroxide

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SECTION 1

INTRODUCTION

Hydrogen chloride (HCl) is one of the major acid gases emitted from municipal and hazardous waste incinerators. The United States Environmental Protection Agency (EPA) is currently regulating emissions of HCl from hazardous waste incinerators under 40 CFR 264.343 to 4 lbs/hr or an HCl removal efficiency of at least 99%. The EPA is also currently considering regulating HCl emissions from municipal waste combustors (MWC's), and several state and local agencies have already set HCl emission limits for new MWC's. In addition, HCl continuous emission monitoring systems (HCl CEMS's) are currently installed or are being installed at certain facilities under state and local pollution control agency requirements.

To support current and future regulations regarding HCl emissions and to determine the relative accuracy of installed HCl CEMS's, a reference method is required to independently determine flue gas concentrations of HCl. The reference method should be free of interferences; in the case of waste incinerators, diatomic chlorine (Cl_2) is an important potential interferent.[1] A methodology has been developed and validated which overcomes the potential bias caused by Cl_2 by collection of HCl using an acidified impinger solution which is unfavorable for Cl_2 collection.

This report presents the results of a laboratory and field research program funded by EPA and conducted by Entropy Environmentalists, Inc. (Entropy) and Research Triangle Institute (RTI) to develop and evaluate a sampling and analysis protocol to measure HCl emissions from incineration processes. Specific phases of the research program were: (1) development of a feasible methodology, based on a literature review, for sampling and analysis of HCl free of Cl_2 interference; (2) laboratory evaluation of the candidate methodology, particularly the sampling procedure to reduce Cl_2 interference; (3) evaluation of the methodology by field testing at a MWC equipped with a state-of-the-art acid gas control system; and (4) confirmatory analyses of the low concentration level HCl cylinders used for the field evaluation test and the higher concentration HCl and Cl_2 cylinders used for the laboratory work.

The initial literature search and selection of a suitable sampling and analytical protocol was conducted by the EPA. The protocol was selected according to demonstrated speciation of HCl and Cl_2 and accuracy of the analytical technique, and secondarily, the availability of equipment, and universality of sampling and analytical techniques.

The protocol was initially evaluated in the laboratory to optimize sample collection. Particular attention was devoted to optimizing the HCl collection

efficiency and minimizing the interference caused by Cl_2. The optimized protocol was also subjected to ruggedness testing in the laboratory.

Two field tests of the protocol were conducted at MWC's to complete the evaluation process. These tests included using the protocol to determine the relative error of CEMS's.

Low concentration level HCl cylinders (less than 60 ppm) used for the field evaluation were analyzed by Research Triangle Institute both before and after use. Higher concentration level HCl and Cl_2 cylinders (greater than 150 ppm) used in the laboratory evaluations of the sampling protocol were analyzed by Entropy following their use.

REPORT ORGANIZATION

Section 2 presents the conclusion and recommendations concerning the draft HCl protocol. The literature search and the selection of potential sampling and analytical protocols are discussed in Section 3. The experimental procedures used for the laboratory evaluation, ruggedness testing, and the field evaluation testing are presented in Section 4. The results of the laboratory evaluations and field evaluation tests are discussed in Section 5. Finally, Section 6 presents the quality control and quality assurance procedures implemented for this study. Appendix A includes the draft HCl method in Federal Register format.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Manual determination of HCl concentrations in municipal waste combustor and hazardous waste incinerator stack gases involves two phases: (1) sample collection and recovery and (2) sample preparation and analysis. The precision of the sampling and analysis method was determined employing simultaneous paired midget impinger sampling trains. The accuracy of the method was estimated by dynamically spiking the sampling train and by comparison to HCl CEMS's. Based on this work, the following conclusions can be made:

- Sampling with a modified Method 6 sampling train followed by analysis using ion chromatography is an acceptable procedure for measuring HCl from municipal waste combustors at levels of 3 to 50 ppm with 21 percent moisture and from gas cylinders at concentrations up to 500 ppm.

- A single midget impinger with 15 ml of 0.1 N sulfuric acid is a very efficient collector of HCl under all conditions tested.

- Chlorine gas in the sample at a level less than 50 ppm does not cause a significant interference with the recommended HCl procedure.

- Preliminary field tests suggest that there is no significant bias in the HCl measurement caused by using a stainless steel probe tip as compared to a glass probe tip.

- Based on the analysis of spiked chloride standards, neither fluorides, bromides, nitrates, nor sulfates interfere with the chloride analysis.

- Reduced reagent volume, extended sampling times, increasing impinger pH, warmer impinger temperatures, and higher flow rates do not have a significant effect on sample collection efficiencies.

- The precision (standard deviation) for the HCl sampling and analysis protocol ranged from 0.24 to 0.49 ppm at flue gas HCl levels of 3.9 to 15.3 ppm.

- The bias of the sampling and analysis protocol was 5.5% and 7.1% for HCl cylinder gas concentrations of 9.7 and 34.3 ppm, respectively.

- The relative errors and biases relative to the manual HCl method for the TECO^{R} HCl CEMS were 1.6% and 6.8%, and 0.07 $\pm$ 0.79 ppm and 0.68 $\pm$ 1.58 ppm, at average flue gas HCl levels of 3.9 and 9.9 ppm, respectively.

- The relative errors and biases relative to the manual HCl method for the Bran and Luebbe® CEMS were 69% and 58%, and -2.66 ± 0.90 ppm and -5.7 ± 2.35 ppm, at average flue gas HCl levels of 3.9 and 9.9, respectively.

- The precisions (standard deviations) for the TECO CEMS were 0.75 ppm and 1.50 ppm at average flue gas HCl levels of 3.9 and 9.9 ppm, respectively. The precisions (standard deviations) for the Bran and Luebbe CEMS were 0.87 ppm and 2.30 ppm at the same flue gas HCl levels.

- Flue gas CO_2 absorption by alkaline impinger reagents was not found to be significant in either the midget impinger train or the Method 5-type train.

- The midget impinger train and the Method 5-type train produced similar HCl results at a flue gas HCl concentration of 21.2 ppm. The Method 5-type train produced significantly lower HCl results than the midget impinger train at a flue gas concentration of 4.8 ppm. The low bias was thought to be caused by unreacted lime collecting in the Method 5-type train and reacting with gaseous HCl from the sample.

Based on the results of this method development and evaluation study, the following are recommended:

- A laboratory evaluation of an air purge of the acidified impingers after sampling should be conducted to see if any of the Cl_2 collected in the acidified impingers could be displaced. This approach would be similar to EPA Method 8 where a 15-minute air purge is conducted after sampling to displace any SO_2 collected in the first impinger.

- A nozzle oriented opposite the gas flow and a Teflon filter can be used with the manual method probe assembly to minimize collection of particulate matter and loss of gaseous HCl through reaction with glass surfaces and alkaline particulate matter. A glass wool plug or a glass fiber filter should <u>not</u> be used to prevent particulate matter from entering the train.

- Further work is needed to determine the reason for the HCl loss in the Method 5 sampling train.

- The acidified impinger method could also be used for measuring Cl_2 emissions by determining the Cl^- catch in the two NaOH impingers.

- HCl CEMS's should be calibrated with HCl cylinder gases of known concentrations to provide accurate results.

- A field evaluation of the manual method and CEMS's for HCl measurement should be conducted at a hazardous waste incinerator.

SECTION 3

METHOD SELECTION

The most commonly utilized sampling protocols for HCl specify either the use of sodium hydroxide solutions in midget impingers[2,3] or sodium bicarbonate/sodium carbonate solutions in Method 5-type impingers.[4] Several titrametric techniques have been evaluated for Cl^- analysis, including the Fajans method,[5] the Mohr method,[6] using a potassium dichromate indicator, the mercuric nitrate method,[7] and the Volhard method.[8] The mercuric nitrate method was found to provide acceptable sensitivity and precision, and was selected for further evaluation. To overcome a high bias caused by sulfite, sample pretreatment with hydrogen peroxide was found to be necessary. The presence of heavy metal cations in the samples also required sample pretreatment through a cation exchange column. Suppressed ion chromatography is specified as the analytical technique for samples collected in the sodium bicarbonate/sodium carbonate impinger solution.[4]

The collection of HCl in an impinger train depends on dissolution of the HCl gas in an aqueous impinger reagent to form the actual analyte, the chloride ion (Cl^-), as follows:

$$HCl + H_2O = H_3O^+ + Cl^- \quad (1)$$

HCl is highly water soluble with the chemical equilibrium favoring Cl^- formation. In contrast, Cl_2 is not nearly as water soluble, but upon hydrolysis will form a proton (H^+), Cl^-, and hypochlorous acid (HClO) according to the following formula:

$$Cl_2 + 2H_2O = H_3O^+ + Cl^- + HClO \quad (2)$$

The degree of Cl_2 hydrolysis is dependent on the pH and the Cl^- concentration of the aqueous solution, with Cl_2 hydrolysis favored in dilute alkaline solutions. Most published methods for HCl[2,3,4] use a dilute alkaline impinger reagent for sampling, followed by Cl^- analysis. With this approach, any Cl^- formed by hydrolysis of Cl_2 in the source emissions is indistinguishable from the Cl^- formed by HCl dissolution, causing a potential for a high bias in the HCl emission measurement. This was recognized by the EPA, and an investigation, "Sampling and Analytical Methods for Halogens in Incinerator Emissions," was conducted by GCA Corporation under Contract No. 68-02-3129, Technical Directive No. 117.[9] The experiments were designed to determine the distribution of HCl and Cl_2 in a midget impinger train, with four impingers connected in series. The first two impingers contained water and the second two impingers contained 0.1 N sodium hydroxide (NaOH) to absorb Cl_2 which could damage the pump. These experiments showed that over 99% of the HCl was

collected in the first water impinger. The Cl_2 was distributed throughout the sampling train with the second water impinger collecting 22% and the first NaOH impinger collecting 77%. The pH of the first water impinger was checked and found to be 1; the low pH was thought to inhibit Cl_2 collection in the first impinger. The pH of the second water impinger was found to be 4; this pH was thought to be high enough to allow collection of some of the Cl_2. These observations lead to the conclusion that acidification of both water impingers to a pH of 1 would enhance the separation of HCl and Cl_2 in the impinger train. Additional experiments were conducted with the first two impingers of the train acidified to a pH of 1 using sulfuric acid. These experiments did show that separation of HCl and Cl_2 occurred in the sampling train; however the following major points were not determined for this sampling protocol:

- The collection efficiency for HCl in the acidified impingers at a high flow rate; and

- The capability of Cl_2 to pass through the acidified impingers at low flow rates.

The experiments described above suggest that the acidified impinger train has the potential to separate HCl from Cl_2. The EPA decided that further laboratory experimentation was needed to determine the answers to the two points listed above and to validate the acidified impinger sampling method.

SECTION 4

EXPERIMENTAL PROCEDURES

This section presents the experimental procedures used to conduct all phases of the evaluation of the draft HCl protocol. It is divided into four subsections concerning the initial laboratory evaluation, the preliminary field test, the ruggedness test, and the field evaluation test.

LABORATORY EVALUATION

The experimental approach for the laboratory evaluation was designed to evaluate the HCl collection efficiency and Cl_2 separation of the sampling method, as well as investigate the interaction of HCl and Cl_2 in the sampling train at different gas concentrations and sample flow rates. The experimental setup used is shown in Figure 1. Gas cylinders containing high levels of HCl and Cl_2 (between 150 and 500 ppm) to simulate worst case conditions were used to produce the gas stream introduced into the impinger trains. Scott® Model 51-17B stainless steel pressure regulators, which are suitable for HCl and Cl_2 service, were used in conjunction with Nupro glands and a nitrogen purge assembly to deliver the gases to the sampling manifold. Stainless steel needle valves were used to control the flow of the gases from the cylinders. Teflon lines and Teflon connectors were used to convey the gases to a glass mixing chamber. From the mixing chamber, the gases flowed into a glass manifold where up to three impinger trains could be connected. Gas flows were set using the needle valves by passing the gases through impingers containing a caustic solution and connecting the impinger outlet to a mass flow meter. During the laboratory evaluation, three midget impinger trains were connected to the glass manifold. A mass flow meter and a dry gas meter were connected to the outlet of each sampling train.

The experimental design used in the laboratory evaluation involved five test conditions. Each test condition involved sampling with three midget impinger trains, and was conducted twice. The first test condition involved sampling an HCl gas mixture at a flow rate of 2 lpm for 20 minutes. The objective of this test condition was to determine the HCl collection efficiency of the first two acidified impingers at a high flow rate (minimum HCl residence time).

The second test condition involved sampling a Cl_2 gas mixture at a flow rate of 0.5 lpm for 20 minutes. The primary objective of this test condition was to determine the ability of the first two acidified impingers to pass the Cl_2 through with a minimum of purging (maximum Cl_2 residence time).

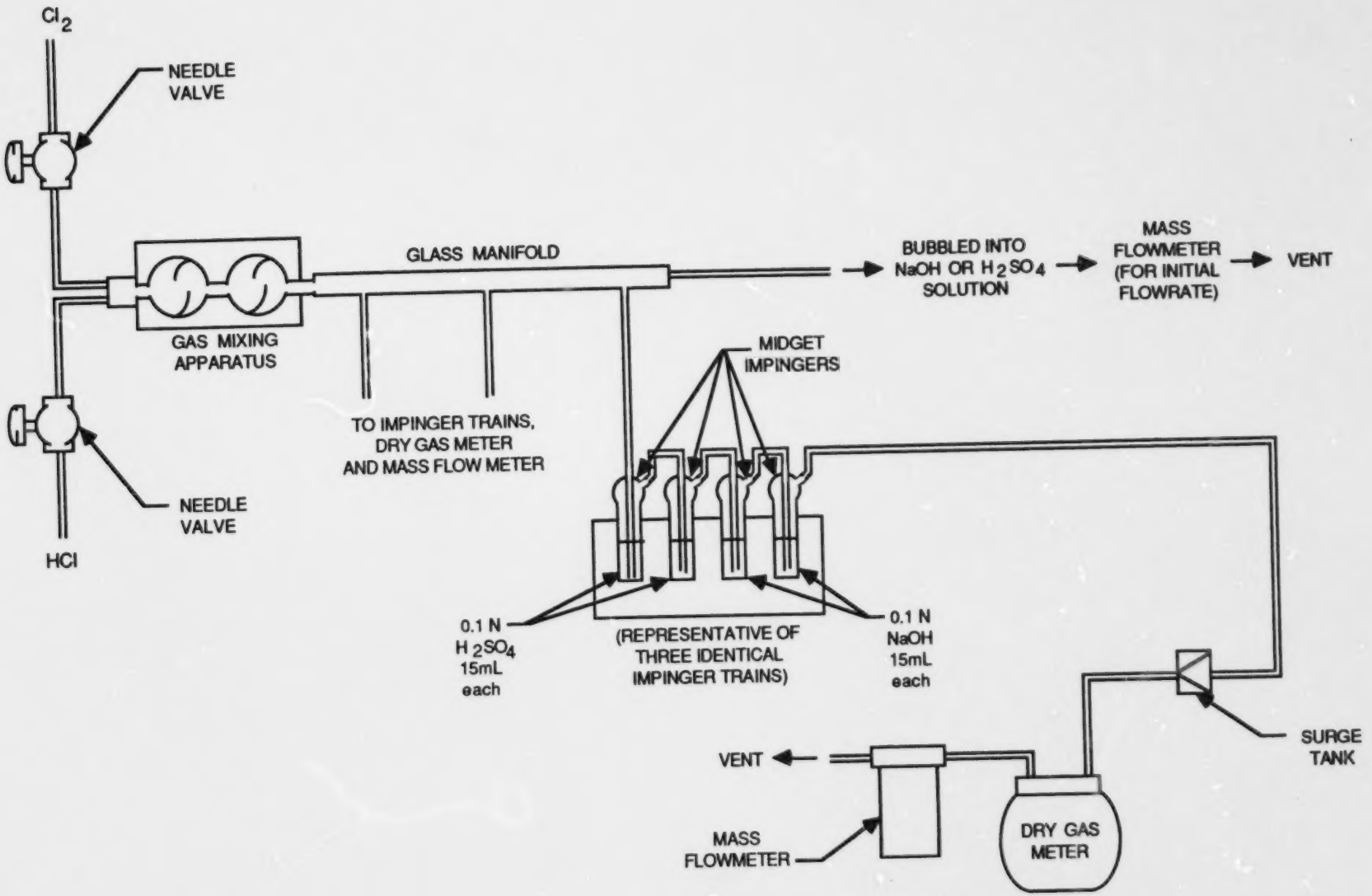

Figure 1. Sample generation system and midget impinger sampling train.

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These first two test conditions allowed (1) determination of the distribution of the resulting Cl^- under conditions least favorable for HCl and Cl_2 speciation, respectively, and (2) determination of the collection efficiency of the sampling train.

The third test condition involved sampling a mixture of high concentration HCl and Cl_2 gases (221 and 197 ppm_v, respectively) at a flow rate of 0.5 lpm for 20 minutes. The objective of this test condition was to determine the ability of Cl_2 to pass through the first two impingers at a low flow rate in the presence of high levels of HCl.

The fourth test condition involved sampling the same mixture of HCl and Cl_2 gas at a flow rate of 2 lpm for 20 minutes. The objective of this test condition was to determine the ability of the first two impingers to retain the HCl at a high flow rate in the presence of high levels of Cl_2.

The fifth test condition involved sampling Cl_2 at a flow rate of 2 lpm for 20 minutes. The objective of this test condition was to determine the distribution of Cl_2 in the entire sampling train at a high flow rate.

To establish the concentration of the HCl and Cl_2 cylinders needed to calculate the collection efficiency, Entropy conducted independent analyses of the gas cylinders. This determination involved sampling using a midget impinger train with 0.1 N NaOH impinger reagent, and analysis of the Cl^- content of the entire train by ion chromatography (IC).

The reagent from each impinger in the experimental trains from the test conditions was quantitatively recovered separately and diluted to 100 ml. The Cl^- concentration of each impinger was determined by IC, with high concentration samples being diluted to reach the analytical range of the IC. The total amount of Cl^- collected in each acidified impinger in the train was used to calculate the HCl concentration using the following formula:

$$ppm_v = \frac{m \times 24.055}{V_{m(std)} \times 35.45} \qquad (3)$$

where:

m = Mass of Cl^- in sample, ug,

24.055 = Ideal gas molar volume at 293°K and 760 mm Hg, liters/g-mole,

$V_{m(std)}$ = Dry gas volume corrected to 293°K and 760 mm Hg, liters, and

35.45 = Mole weight of Cl^-, ug/ug-mole.

The total amount of Cl^- collected in both NaOH (basic) impingers was calculated using the following formula:

$$ppm_v = \frac{m \times 24.055}{V_{m(std)} \times 70.90} \times 2 \qquad (4)$$

where:

m = Mass of Cl^- in sample, ug,

24.055 = Ideal gas molar volume at 293°K and 760 mm Hg, liters/g-mole,

$V_{m(std)}$ = Dry gas volume corrected to 293°K and 760 mm Hg, liters, and

70.90 = Mole weight of Cl_2, ug/ug-mole, and

2 = Stoichiometric conversion factor, moles of Cl^-/mole of Cl_2.

Collection efficiency for HCl was calculated based on the calculated HCl concentration and the expected HCl concentration using the following formula:

$$\text{Collection Efficiency (\%)} = \frac{ppm_{v(found)}}{ppm_{v(expected)}} \times 100\% \quad (5)$$

where:

$ppm_{v(found)}$ = ppm_v of HCl found in the first two acidified impingers, and

$ppm_{v(expected)}$ = ppm_v of HCl expected in the first two acidified impingers based on the proportion of HCl and Cl_2 in the gas mixture sampled and the independently measured concentration of the HCl cylinder.

The collection efficiency for Cl_2 was calculated in a parallel manner.

PRELIMINARY FIELD TEST

After completion of the initial laboratory evaluation, an opportunity arose to collect preliminary HCl field samples at a mass-burn municipal waste combustor (MWC) using the candidate method. HCl samples collected using a manual method were needed to evaluate an HCl continuous emission monitoring system (CEMS). This provided an opportunity to determine how well the proposed sampling method responded to changes in the effluent HCl concentrations relative to the HCl CEMS and to identify additional variables to be explored during the ruggedness test. This preliminary field sampling, using conditions considered optimum for the proposed method, also allowed evaluation of the IC analysis procedure by challenging it with interferences present in the MWC emissions.

Specific objectives of the test were: (1) to collect samples from a MWC to identify any potential problems with the sampling and/or analytical methods when used at a typical HCl emission source, (2) to determine how well the sampling method responds to changes in the effluent concentration by comparing the sampling results to the results determined by the HCl CEMS's, and (3) to determine if the use of a stainless steel probe tip as opposed to an all glass sampling probe affects the sampling results.

The MWC tested represented the state-of-the-art in acid gas control technology; the levels of HCl in the stack gas were 20- to 100-times lower than those used in the laboratory evaluation. The HCl samples were collected at the breeching between an induced-draft fan and the stack. This sampling location is downstream of the dry lime scrubber/fabric filter acid gas control device. The center port on the breeching was used. The sampling probe for the HCl CEMS was installed in the upper sampling port at this location. The CEMS was a Bodenseewerk Spectran Model 677 utilizing the principle of infrared absorption. Previous testing at this location demonstrated that there was no stratification occurring in the breeching.

The configuration of the HCl sampling train used included a glass-lined heated probe, midget impingers in an ice water bath, and a Method 6 meter box equipped with a Singer dry gas meter as shown in Figure 2. A heated three-way glass stopcock was installed directly between the probe outlet and the first impinger inlet. This stopcock permitted the sampling probe to be purged with stack gas, using the vacuum pump, prior to collecting samples. The impinger train consisted of two impingers, each containing 15 ml of 0.1 N H_2SO_4 followed by a single impinger containing 15 ml of 0.1 N NaOH and a Mae West impinger containing Drierite.

A 30-minute sampling time was used for the nine runs to determine the relative error of the HCl CEMS's. The sampling time was extended to one hour for the six comparative test runs. The sampling rate for all trains was 2 lpm. The moisture content of the flue gas was determined using Alternative Method 4 and the flue gas temperatures, using procedures in Method 2.

For the probe tip comparison test runs (Nos. 4, 5, and 6), paired sampling trains were used. One train sampled with a glass-lined probe with a stainless steel tip and the other train sampled with a glass-lined probe with the liner extending 3 inches beyond the end of the probe sheath.

For the first four comparative test runs and the first, fifth, and ninth relative error runs, all three impingers of each train were recovered separately and diluted to 100 ml. For the remaining runs, the impingers were recovered together and diluted to 100 ml. All samples were returned to Entropy's laboratory for IC analysis using single column ion chromatography (SCIC).

The non-suppressed IC was performed with a Perkin-Elmer Series 10 pump, a Rheodyne Series 7010 sample injection valve, a 100 x 4.1 mm Hamilton PRP-X100 anion column, and a Milton Roy detector with a temperature-controlled conductivity cell. The eluent was 4 mM potassium hydrogen phthalate at a flow rate of 2 ml/min. An electronic integrator was used to produce chromatograms and provide integration of the Cl^- peak area. The system was calibrated before and after each analysis. A spreadsheet program was used to calculate the calibration line, sample results, and flue gas HCl concentrations.

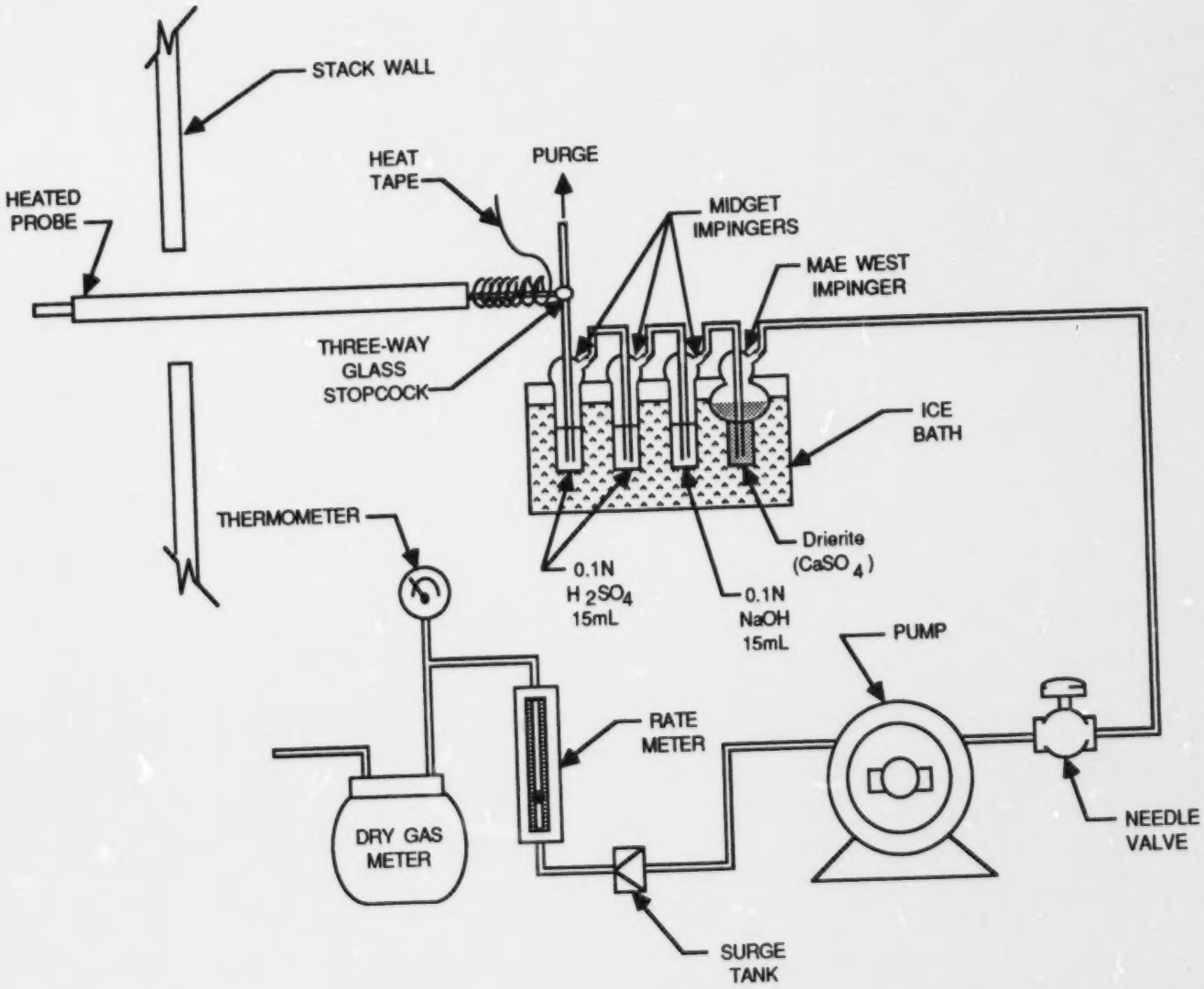

Figure 2. Configuration of acidified impinger sampling train for collection of preliminary field samples.

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RUGGEDNESS TEST

The results of the laboratory evaluation of the proposed HCl method and the preliminary field test were used to identify the optimum HCl sampling conditions minimizing interference from Cl_2. The method was then assessed using a ruggedness test based on a design patterned after that described by Aden.[10] It involved selecting six variables plus a blank and using different combinations of these variables in conducting 8 test runs with duplicate sampling trains. The combinations of the variables were arranged in a restricted manner to allow the necessary computations to identify which variable had a significant effect on the results.[10]

The optimum HCl sampling conditions and the variations made from the optimum conditions are shown in Table 1. The optimum conditions are indicated with an asterisk. A blank was included in the experimental design to determine if the method was in control.

For the ruggedness test, duplicate sampling trains were used to sample HCl and Cl_2 cylinder gas mixtures. The procedures for sampling and the determination of actual HCl cylinder gas concentrations were parallel to those used in the initial laboratory evaluation. The first and second impingers (H_2SO_4) were recovered separately and the third and fourth impingers (NaOH) were combined. The impinger samples were analyzed by ion chromatography and results were expressed as a percent recovery of the HCl in the first and second impingers. While the results for the third and fourth impingers were not included in the HCl recovery calculation, they were useful in investigating the cause of any significant effect of a particular variable.

An average was calculated for the results for the duplicate sampling trains for each run. For each variable, the results were averaged for the optimum conditions and the varied conditions. The difference between the two average values were indicative of whether the sampling method is sensitive to the change in that value.

Following the procedure described by Wernimont,[11] a standard deviation was calculated for the difference between the duplicate sampling train runs for all eight runs. This standard deviation was used to calculate the standard error for the differences between averages of the results for the eight conditions. From this standard error, a confidence interval was calculated using seven degrees of freedom.

FIELD EVALUATION TEST

The field test evaluation of the proposed HCl measurement methodology was conducted at a second state-of-the-art MWC. The facility was selected because the low HCl effluent levels are typical of a modern MWC with an acid gas control system. The primary objectives of this field test were to concurrently determine the bias of HCl CEMS's and to determine the precision and estimate the accuracy of the HCl manual method. The specific objectives were:

TABLE 1. RUGGEDNESS TEST EXPERIMENTAL DESIGN

Variable[a]	Test Run No.							
	1	2	3	4	5	6	7	8
Sample flow rate (lpm)	2.0*	2.0*	2.0*	2.0*	2.5	2.5	2.5	2.5
Sampling time (min)	20*	20*	60	60	20*	20*	60	60
First impinger pH	1.0*	2.0	1.0*	2.0	1.0*	2.0	1.0*	2.0
Impinger temperature[b]	Ice*	Ice*	Amb	Amb	Amb	Amb	Ice*	Ice*
Chlorine concentration (ppm)	0*	50	0*	50	50	0*	50	0*
Reagent volume (ml)	15*	10	10	15*	15*	10	10	15*
Blank	no variation							

[a] Optimum conditions indicated by *.

[b] Amb = ambient temperature, approximately 85°F; Ice = temperature of ice water bath.

- Determine the bias of three HCl CEMS's at the normal HCl flue gas level (approximately 4 ppm) and at an elevated level (approximately 15 to 20 ppm) employing the proposed HCl measurement methodology.

- Determine the precision of the entire sampling and analysis procedure by comparing the results of co-located, simultaneously operating midget impinger sampling trains.

- Estimate the accuracy of the entire sampling and analysis procedure by dynamically spiking the sampling train with HCl gas from cylinders whose concentrations were independently determined.

- Determine the significance of flue gas carbon dioxide (CO_2) absorbance in the alkaline impinger reagents relative to the measured gas sample volume.

- Compare the results of co-located, simultaneously operating sampling trains consisting of the proposed HCl sampling methodology and a sampling methodology based on a Method 5-type train.

The test matrix shown in Table 2 was used to collect data to meet these objectives. Specifically, five sets of different test comparisons were performed during the field evaluation. The initial test set (Day 1) was conducted to determine the amount of CO_2 removed from the flue gas sample by the alkaline impinger reagents. The significance of this CO_2 removal relative to the measured gas sample volume had to be determined prior to conducting the remaining test sets to determine if correction of the measured gas sample volume would be necessary.

The test set conducted on Day 3 was the comparison of the proposed HCl sampling train to a modified Method 5 sampling train with 0.1 N NaOH replacing water as the impinger reagent. The first run was conducted isokinetically, the second run was conducted non-isokinetically at a higher sampling rate of 0.75 cfm. This comparison was of interest due to the common use of the Method 5 train for HCl sampling and the potential for combining HCl sampling with particulate sampling.

The third and fourth test sets (conducted on Days 4 and 5) were designed to concurrently determine the bias of three HCl CEMS's and the precision of the proposed HCl sampling method. The third test set consisted of ten runs to determine the monitor relative error using paired midget impinger trains while the facility was operating normally. The fourth test set consisted of six similar runs, also using paired trains, conducted while the facility was operating with higher acid gas emissions, but still within their permit limits for HCl and SO_2. The final test set involved dynamically spiking paired midget impinger trains through the probe assembly with HCl from gas cylinders to estimate the accuracy of the proposed HCl method. The first set of dynamic spike runs conducted on Day 2 was invalidated because of an over-pressurized manifold. The second set was conducted successfully on Day 6. Two low concentration HCl cylinders were used with three spiking runs per cylinder (see later section on "Analysis of Spiking Cylinders").

TABLE 2. TEST MATRIX FOR FIELD EVALUATION TEST

Test Day	Test Run AM	Test Run Noon	Test Run PM	Analytical
1	MI, MI	MI, MI	MI, MI	Cl^-, H_2O, CO_2
		M3	M3	CO_2
	M5-OH		M5-OH	Cl^-, H_2O, CO_2
2	Dynamic spike of paired MI trains with HCl cylinder gas; performed in triplicate at two concentrations (invalidated - repeated on Day 6)			Cl^-
3	MI, MI		MI, MI	Cl^-, H_2O
	M5-OH, M5-OH		M5-OH, M5-OH	Cl^-, H_2O
4	10 runs to determine CEMS relative error using paired MI's at low flue gas HCl			Cl^-, H_2O
5	6 runs to determine CEMS relative error using paired MI's at elevated flue gas HCl			Cl^-, H_2O
6	Dynamic spike of paired MI trains with HCl cylinder gas: performed in triplicate at two concentrations			Cl^-

MI - Draft method midget impinger train with knockout impinger and a rigid, heated Teflon filter in front of the first 0.1 N H_2SO_4 impinger and ice water bath.

Cl^- - Chloride analysis by ion chromatography.

H_2O - Moisture determination by Alternative Method 4 for midget impinger trains and by Method 4 for Method 5 trains.

CO_2 - For all MI and M5-OH trains, CO_2 absorption determination (as bicarbonate) in alkaline impinger reagent by ion exclusion chromatography.

M3 - EPA Method 3 for CO_2.

M5-OH - EPA Method 5 train with 0.1 N NaOH impinger reagent.

Facility Description

The Millbury Resource Recovery Facility operates two identical mass-burn municipal waste combustors (MWC's). A schematic of one of the combustors is presented in Figure 3. Each combustor can handle up to 750 tons per day of municipal solid waste and is equipped with a state-of-the-art spray dryer absorber (SDA) for acid gas removal and a three-field electrostatic precipitator (ESP) for particulate control.

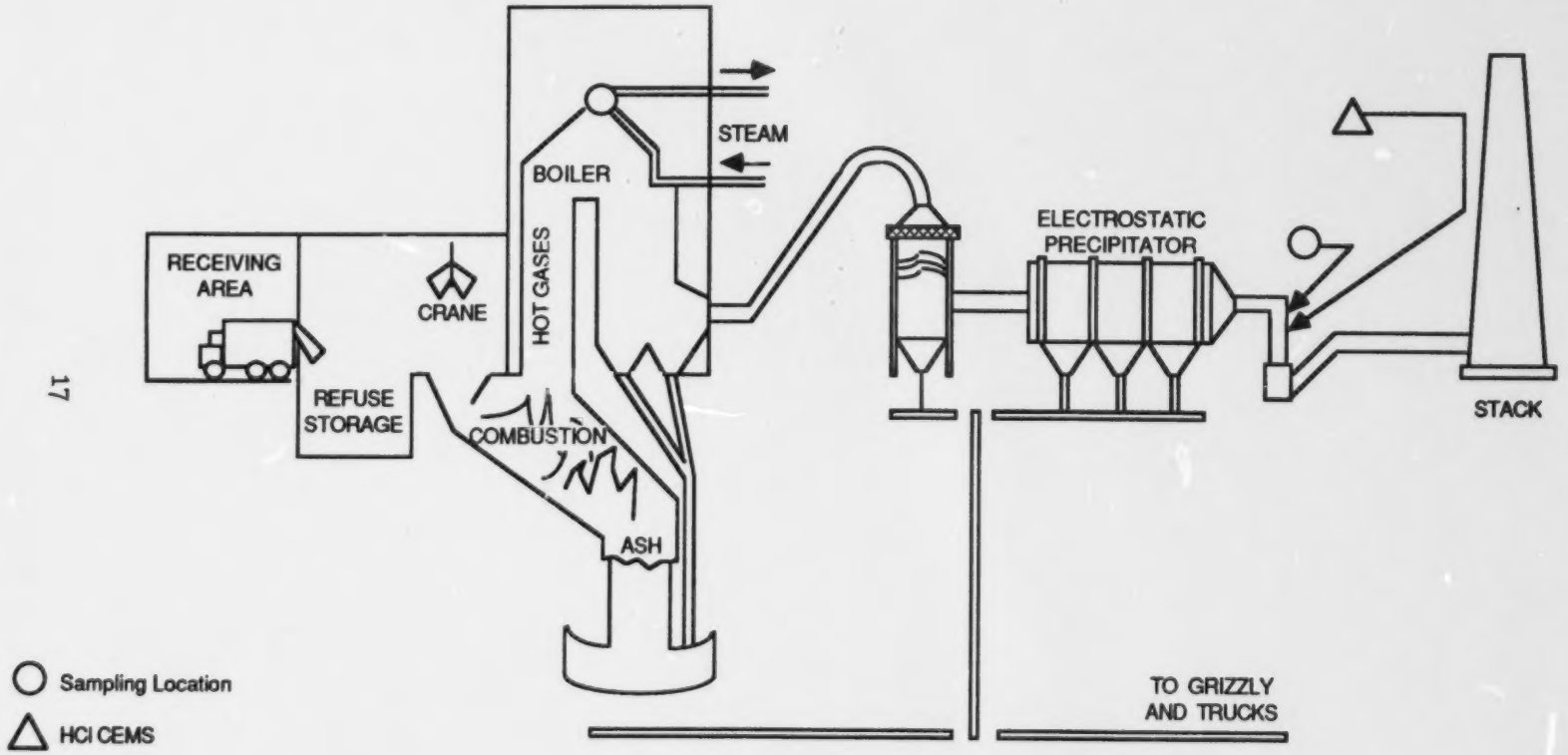

Figure 3. Schematic of a combustor at the Millbury Resource Recovery Facility.

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Sampling Location

The HCl sampling was performed at the ESP outlet upstream of the induced draft (ID) fan. There were sampling systems for three HCl CEM's installed in two neighboring sampling ports at this location. The HCl CEM's were being operated by Entropy under contract to the U. S. EPA, EMB as part of a long-term monitoring project in support of the EPA's MWC emission study. A schematic of the ESP outlet test location is shown in Figure 4. The test location has 5 horizontally arranged 4-inch ports located in accordance Method 1 requirements for flow determination. The test location also has a generous sampling platform with sufficient space to accommodate the test personnel and equipment required to conduct the field tests.

Sampling Equipment and Train Configuration

The quadruplicate-train sampling system included four heated glass-lined sampling probes used to provide an individual gas sample to each impinger train. The probe assembly was fitted with an S-type pitot and a thermocouple to measure the flue gas velocity and temperature. The outlet ends of all four probes were mounted into a heated box where the Method 5 glass-fiber filters (Whatman® EMP 2000) were housed. Stainless steel nozzles were fitted to the two probe assemblies connected to the Method 5 trains. On the two midget impinger train probes, an in-stack filter employing a 25 mm Teflon filter with a 1.0 um pore size (Schleicher and Schuell®, 41-01510) was fitted to the inlet of the glass probe liner and secured with a Teflon compression union.

A heated three-way glass stopcock was connected between the outlet of each midget impinger train probe and each midget impinger train. On the third leg of each stopcock a purge line was attached. Each purge line had a drying tube and a rotameter in series in front of a small diaphragm pump to purge each probe and stopcock for 5 minutes immediately prior to sampling with flue gas at a purge rate of at least 2 liters/minute.

The impinger sequence for the midget impinger train was: an impinger with a shortened stem to act as a knockout impinger for moisture, two impingers each containing 15 ml of acidified water (0.1 N H_2SO_4), one impinger containing 15 ml of 0.1 N NaOH, and one Mae West impinger containing Drierite (see Figure 5). The second NaOH impinger previously used was eliminated to permit moisture determination. Method 6 meter boxes equipped with calibrated Singer dry gas meters were used to measure the gas sample volume pulled through each midget impinger train.

The impinger sequence for the Method 5-type train was a Smith-Greenburg impinger containing 100 ml of 0.1 N NaOH; a modified Smith-Greenburg impinger containing 100 ml of 0.1 N NaOH; an empty modified Smith-Greenburg impinger; and an impinger containing 200 g of indicating silica gel. Calibrated Method 5-type meter boxes were employed to measure the gas sample volume pulled through the Method 5 impingers and to monitor the flue gas velocity.

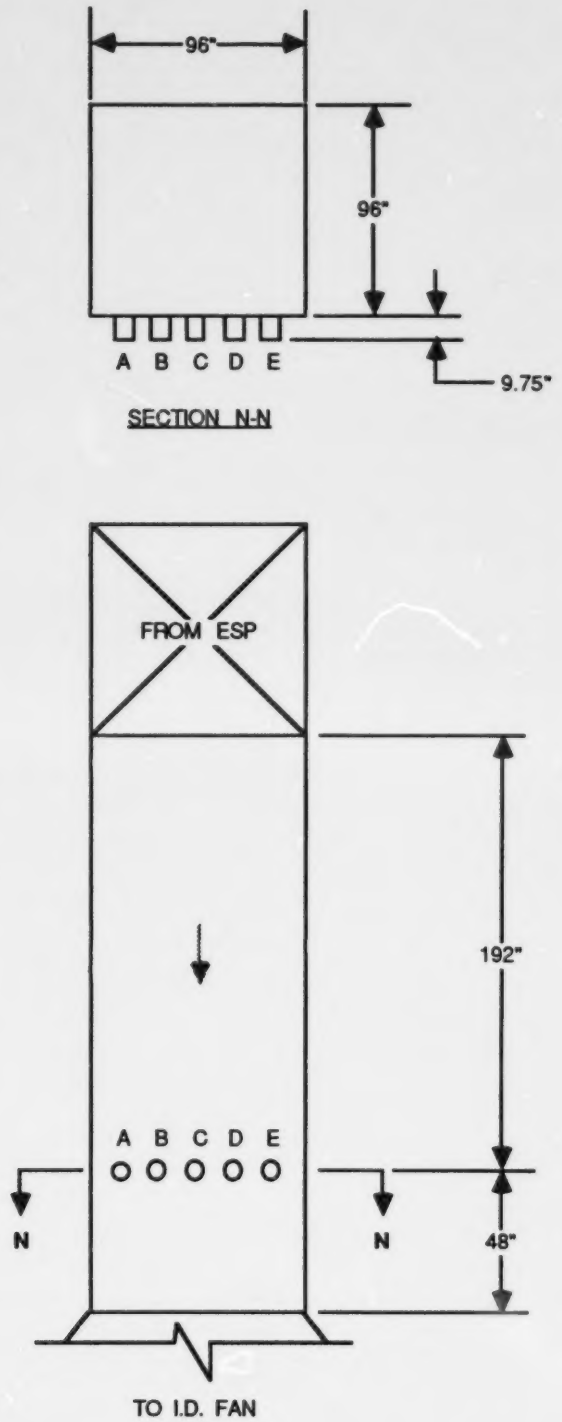

Figure 4. Schematic of the ESP outlet sampling location.

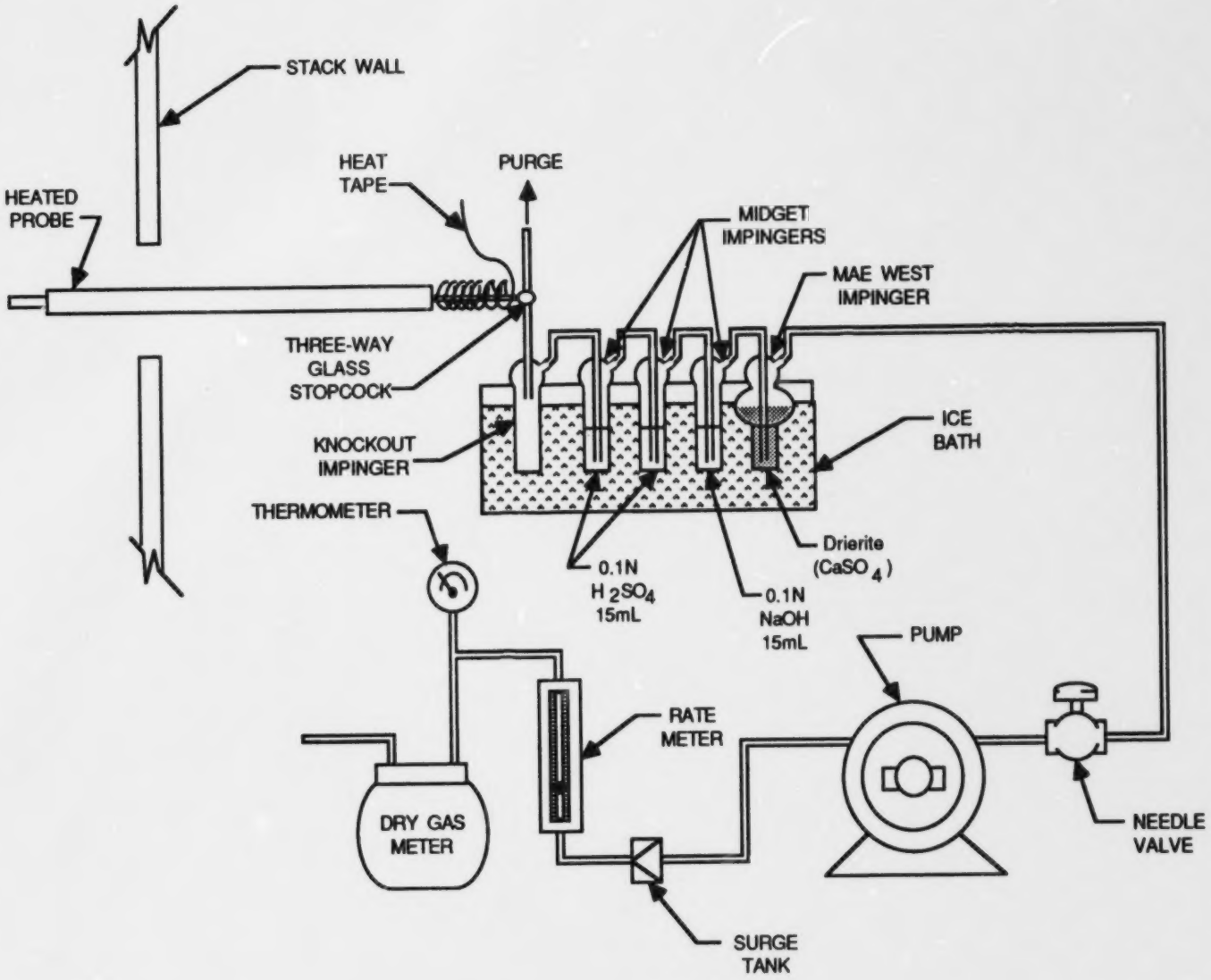

Figure 5. Schematic of midget impinger train.

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Flue Gas Molecular Weight Determination

The integrated sampling technique described in EPA Method 3 was used to obtain a composite flue gas sample for fixed gas (O_2, CO_2) analysis. A small peristaltic pump and a stainless steel probe were used to extract a single point flue gas sample, which was collected in a Tedlar bag. Moisture was removed from the gas sample so that the fixed gas analysis was on a dry basis. The composition of the gas sample was determined using an Orsat analyzer.

Continuous Emission Monitoring Systems

Bran and Luebbe Ecometer HCl Monitoring System --

A Bran and Luebbe Ecometer HCl monitoring system was installed at the ESP outlet sampling location. The Ecometer was operated at a range of 0-60 ppm HCl and the HCl emissions did not exceed this measurement range during the test program.

The Ecometer operating principle, based on potentiometric measurement using an Cl^- ion-selective electrode, is as follows: A gas sampling system employing a stainless steel probe to extract a gas sample from the stack, filters and transports the stack gas to the Ecometer. A glass fiber filter is installed at the outlet of the probe to filter particulate matter. Both the probe and the filter are thermostatically heated to 200°C. A flexible heat-traced Teflon line and special diaphragm pump are employed to transport the gas sample from the stack to the analyzer at a flow rate of approximately 1 liter/minute. The gas sample is kept at approximately 200°C prior to absorption to prevent condensation of water vapor in the sample lines, resulting in a loss of HCl.

The flue gas sample is chemically treated, resulting in the absorption of HCl and the formation of Cl^- ions. The chemical solution used to absorb HCl also buffers the pH and ionic strength of the absorbed solution and destroys possible undesirable interferences. The absorbing solution containing the Cl^- ions is degassed and conveyed to the ion-selective electrode to be quantified. After necessary amplification and conversion, a voltage signal proportional to the amount of Cl^- present is produced.

The Ecometer performs an internal calibration routine either automatically or by manual actuation. During the calibration routine, flue gas sampling is stopped and two calibration solutions are fed to the ion-selective electrode in sequence. The calibration results are stored in an internal microcomputer, and used for calculation of the subsequent stack gas measurement results. There are no provisions in the Ecometer system for the introduction of HCl cylinder gas.

The Ecometer measurement is made on a wet basis. The vendor claims the accuracy of the Ecometer to be $\pm$ 5% of full scale and the system response time to be less than 200 seconds.

The output of the Ecometer was fed to Entropy's data acquisition system (DAS) where the signal was converted to a concentration value. The DAS displayed the concentration value continuously on the system's monitor, and stored the one-minute averages on magnetic media. The DAS was programmed to provide 15-minute averages of the one-minute values during the test program.

Thermo Electron Model 15 HCl Analyzer/Model 200 Dilution System --

The Thermo Electron (TECO) Model 200 dilution probe was also installed at the ESP outlet sampling location and connected to a TECO Model 15 HCl analyzer to provide continuous real time measurement of HCl on a wet basis. The TECO HCl CEMS works as follows: The TECO Model 15 employs gas filter correlation (GFC) to measure HCl by infrared (IR) absorption. GFC employs a correlation wheel consisting of two hemispherical cells, one filled with HCl and the other filled with nitrogen (N_2). Integral with the correlation wheel is a chopper pattern necessary to produce the high frequency compatible with the IR detector. Radiation from the IR source is chopped and then passed through the correlation wheel, alternating between the HCl cell and the N_2 cell. The radiation then passes through a narrow bandpass interference filter and enters a multiple optical pass sample cell where absorption by the sample gas occurs. The HCl gas cell in the correlation filter provides a reference signal that cannot be attenuated by the HCl in the gas sample. The N_2 cell is transparent to the IR radiation and therefore produces a measurement beam which can be absorbed by HCl in the sample cell. The chopped detector cell is modulated by alternation between the two gas filters with an amplitude related to the concentration of HCl in the sample cell. Other gases in the sample cell do not cause modulation of the detector signal, since they absorb the reference and measurement beams equally.

Because IR absorption is a non-linear measurement technique, the instrument electronics convert the basic analyzer signal into a linear output. The exact calibration curve is stored in the instrument's microcomputer memory and is used to linearize the instrument output over all ranges. The microcomputer is also used to process signals from both a pressure and a temperature transducer to make corrections to the instrument output, resulting in HCl concentration measurements that are unaffected by changes in the temperature or pressure of the sample gas.

The analyzer has 10 selectable operating ranges from 0-5 ppm to 0-5000 ppm HCl. The analyzer was operated on the 0-5 ppm range. The vendor claims that the detection limit for this instrument is 0.1 ppm. The output of the analyzer was fed to the DAS described above.

The Model 200 dilution system was employed to provide a flue gas sample to the analyzer with a moisture content well below the moisture dew point. The dilution system was comprised of an in-situ dilution probe with a sample orifice, transport tubing for dilution air, calibration gases, diluted sample gas, and vacuum downstream of the sample orifice, and the stack probe control unit. The dilution probe extracted a small amount of flue gas continuously through a fine filter. The flue gas sample flow rate was precisely controlled within 2% by a glass critical orifice with a low coefficient of expansion. The

pressure downstream of the critical orifice was reduced to a vacuum of 0.46 bar with an aspirator driven by the dilution air. The flue gas sample drawn through the critical orifice by the aspirator vacuum was thoroughly mixed with aspirator air, and then transported through the sample line to the analyzer.

The dilution system was adjusted to provide a 12-to-1 dilution ratio employing a 500 cc/minute critical orifice. The dilution ratio was verified by flowing known concentrations of carbon monoxide (CO) through the dilution system to a calibrated CO analyzer. With the 12-to-1 dilution ratio, the in-stack HCl detection limit for the TECO analyzer was 1.2 ppm.

All calibrations of the TECO analyzer and the MDA analyzer (described below) were made by introducing HCl gas through the calibration line to a point within the probe upstream of the fine filter prior to the critical orifice. By this method, the calibration gases followed all the sample conditioning and dilution steps experienced by flue gas samples. The span gas for the calibration routine had an HCl concentration of 47.0 ppm. A check of the calibration curve was made using a midpoint HCl gas with a concentration of 18.4 ppm. The HCl gas cylinder values were established by independent analysis by RTI. Calibrations were performed each morning, and a posttest zero and span drift check were conducted at the end of each test day, but the data was not corrected for drift.

MDA Model 7100 HCl Gas Analyzer --

The MDA 7100 analyzer's detection technique is colorimetric-based, and uses dry reaction substrates formulated for HCl gas contained on a paper tape (Chemcassette detection media). The flue gas sample and calibration gases were provided to the MDA 7100 by the TECO Model 200 dilution system through a heated glass manifold.

The MDA 7100 works on the following principle: A pump within the MDA analyzer draws a gas sample at a constant rate through the Chemcassette media. The HCl in the gas sample reacts with the chemicals impregnated on the Chemcassette paper tape, and forms a colored stain with an intensity proportional to the HCl gas concentration. An electro-optical sensing system reads the stain, and produces an analog signal. The analog signal is converted to a digital signal, compared to calibration values stored in the analyzer's microcomputer, and a concentration value is determined. The output of the MDA 7100 was fed to the DAS described above.

The instrument's operating range was 0-100 ppm (wet basis). The vendor claims that it has a detection limit of 0.2 ppm. At a 12-to-1 dilution ratio with the TECO 200 dilution system, the in-stack HCl detection limit was 2.4 ppm.

Calibration of the MDA 7100 was performed simultaneously with the TECO Model 15 as described above.

Sampling Procedures

All sampling was conducted at a single point in the ESP outlet duct since particulate measurement was not an objective and traversing would have been difficult with the quad-train sampling system. All midget impinger sampling was conducted non-isokinetically at a constant rate of 2 liters/minute. For the first sampling run comparing the midget impinger train to the Method 5 train and the carbonate determination, the Method 5 sampling was conducted isokinetically and, for the second comparison run, the Method 5 sampling was conducted non-isokinetically at a constant rate of 21 liters/minute. For the quad-train runs, the sampling time was one hour and, for the determination of the CEMS relative error and the carbonate determination runs, the sampling time was 30 minutes.

The recovery procedures for the Method 5-type trains involved separate recovery of each impinger along with determination of the moisture collected in each impinger. After the volume of the contents of each impinger was determined, each impinger and corresponding connecting glassware was rinsed with DI H_2O and this rinse added to the impinger solution. The final volume of each impinger sample was determined prior to transferring the sample to a storage container. The front half components, the probe and filter, were handled following the Method 5 procedure, except that the filter and front half rinses were archived and not analyzed.

For the moisture determination employing the midget impinger train following Alternative Method 4, the train was assembled and the entire train weighed prior to sampling. Immediately after sampling the entire train was weighed again.

The midget impinger trains were recovered as follows: the contents of the knockout impinger and the first acidified impinger and the rinse of the two impingers were combined. The contents of the second acidified impinger and the impinger rinses and the contents of the 0.1 N NaOH impinger and the impinger rinses were recovered separately. All samples volumes were adjusted to 100 ml with deionized water.

Dynamic Spiking

To estimate the accuracy of the proposed HCl method, pairs of midget impinger trains were dynamically spiked using low concentration level HCl cylinder gases. The dynamic spiking system consisted of HCl gas cylinders, an HCl gas delivery system, a glass manifold, and a gas chromatograph/electrolytic conductivity (GC/ELCD) system.[12] The delivery system included new Scott® Model 51-17B stainless steel regulators configured with Nupro® glands and a dry nitrogen purge assembly. Regulators were dedicated to each cylinder as past experience showed that a regulator may require up to one hour of flowing HCl gas to reach equilibrium and this equilibrium may be disrupted if the regulator is removed from the cylinder. A glass manifold was used to distribute the HCl gas to the two probes connected to the midget impinger trains. The midget impinger quad-train probes and hotbox were heated to 250°F to simulate stack conditions. The flow rate of excess HCl gas leaving the manifold was monitored to provide sufficient gas to the impinger trains without over-pressurizing the

manifold. The gas purged through the manifold, probes, and stopcocks prior to sampling with the impinger trains was monitored using a GC/ELCD.[12] The GC/ELCD provided real time analysis of the HCl gas stream to assure the delivery system and glass manifold had reached equilibrium with the HCl gas stream.

The analysis of the HCl gas using the GC/ELCD required some modification of available instrumentation. The commercial ELCD used, a Tracor Model 700A, is commercially utilized for analysis of halogenated organics. After separation on a GC column, the chlorinated organics enter a catalytic reactor tube where they are oxidized to form HCl and other oxidation products. The HCl is scrubbed from the effluent exiting the catalytic reactor, forming a chloride solution. Finally, the scrubbing solution containing the Cl^- enters the conductivity cell where it is quantified. For analysis of HCl, the catalytic reactor was bypassed and the carrier gas flow was conducted directly to the conductivity cell where the HCl was scrubbed out using 2-propanol. The solvent flow through the reactor was maintained at about 10 ml/min.

The same midget impinger train sampling procedures and sample recovery techniques as previously described for sampling at the ESP outlet were used for the dynamic spiking experiment. The analytical procedures are described in a later section.

Two low concentration HCl gas cylinders were used for the dynamic spiking, 9.7 and 34.3 ppm. The concentrations of these and five other cylinders were determined both before and after the field test through independent analysis by RTI as described below.

Analysis of Dynamic Spike Cylinders -- [13]

Seven low concentration HCl cylinders were prepared by Scott Specialty Gases at nominal levels of 10, 20, 30, 40, 45, and 55 ppm HCl. All were analyzed at least twice in triplicate using impinger trains both before and after they were taken to the field.

The system used to deliver the HCl from the cylinders to the impingers is shown in Figure 6. It was designed to include inert and/or fresh metal surfaces and allowed for dry nitrogen purging of (1) all water vapor prior to entry of HCl and (2) all HCl prior to opening the system to humid air. All low level HCl cylinders had standard valves accepting Supelco Model 51-17B regulators. A stainless steel "T" served as the interface between the gland and the regulator. A stainless steel tube led from the regulator to a glass manifold with four exit ports. The gland, "T," regulator, and tubing used were new and had not previously been exposed to HCl or any other potentially corrosive gases. The regulator used had a diaphragm of 316 stainless steel, seals of Kel-F and Teflon, and a seat of Monel. The side arm of the "T" was connected to a tank of dry nitrogen through a check valve and also a manual valve that was open only during the process of purging the HCl delivery apparatus described. Three pairs of impingers were connected directly to the manifold via ground glass joints during sample collection. Downstream of each pair of impingers was a calibrated wet test meter to record total volume collected, a mass flow controller to control flow, and a vacuum pump. Two-way stainless steel valves were placed between the wet test meters and the flow

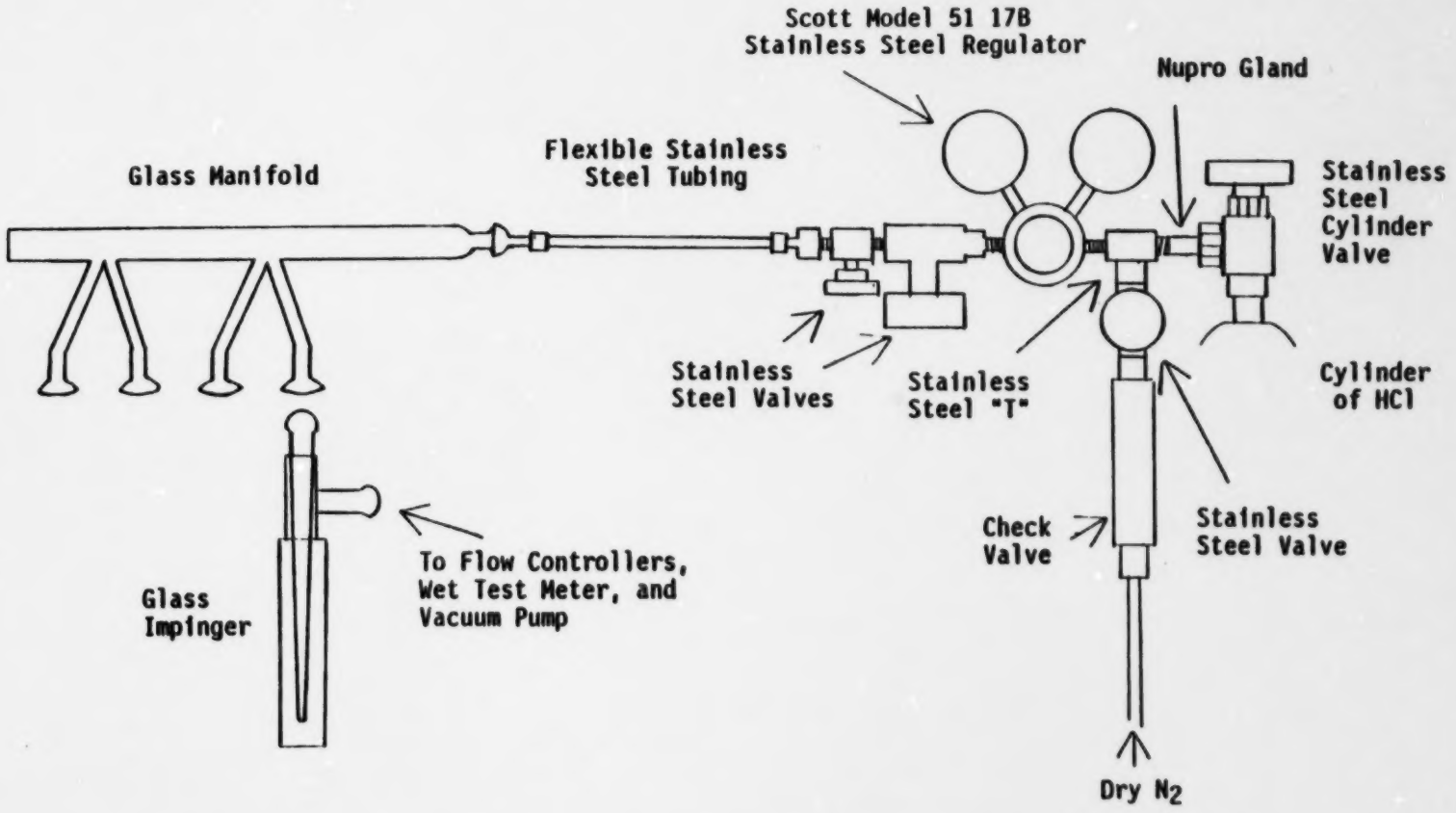

Figure 6. HCl cylinder gas delivery and sample collection system.[13]

controllers. The pumps were started and the values were set such that air was drawn through the controllers. After the controllers stabilized, the valves were set such that the HCl gas was drawn through the impingers.

Deionized water, which has been demonstrated to have a collection efficiency of 99.7 percent,[14] was used to collect the HCl gas cylinder samples. The total HCl cylinder gas flow to the manifold was 3 lpm during sampling. The flow rate through each sampling train was 0.5 lpm which minimized the use of gas while still permitting reproducibility. Sampling was conducted for 20 minutes which was the minimum time necessary to allow the pumps, flow controllers, and wet test meters to stabilize without significant effect on the volume metered.

The impinger solutions recovered were analyzed for chloride using a Dionex 2120i ion chromatograph with a Dynamic Solutions data acquisition system. Standard anion conditions were used. Impinger solutions were diluted such that final solution concentrations of 5 to 20 ppm chloride resulted. The ion chromatographic system was calibrated at the start of each analysis session using four to five standards prepared with KCl in the same matrix as the diluted samples; a calibration check was made at mid-day and the system was recalibrated if the calibration changed more than 5 percent. Blank impinger solutions were analyzed and 20 percent of all impinger solutions were analyzed in duplicate.

The results for the cylinder analyses were averaged and standard deviations were calculated for each set of triplicate analyses. A summary of the pre- and post field test cylinder analysis data is shown in Table 3. The cylinders actually used in the field evaluation are indicated by a triple asterisk.

Analytical Procedures

The field samples collected were analyzed on-site for Cl^- by ion chromatography (IC) and for carbonate (CO_3^{2-}) by ion exclusion chromatography (IEC).

Ion Chromatography Analysis --

Chloride analysis of the midget and Method 5 impinger samples was performed by IC. Non-suppressed IC was performed with a Perkin-Elmer Series 10 pump, a Rheodyne Series 7010 sample injection valve, a 100 x 4.1 mm Hamilton PRP-X100 anion column, and a Milton Roy detector with a temperature-controlled conductivity cell. The eluent was 4 mM potassium hydrogen phthalate and the eluent flow rate was 2 ml/minute. A Spectra Physics electronic integrator was used to produce chromatograms and provide integration of the Cl^- peak area. A Lotus spreadsheet was used to calculate the slope and y-intercept for the linear regression equation of the standards, calculate percent deviation of the standards from the calibration line, calculate sample results as total HCl, and, using the gas sample volume, calculate the flue gas HCl concentrations.

TABLE 3. COMPARISON OF PRE-FIELD TEST AND POST-FIELD TEST CONCENTRATIONS

Cylinder Number	Target Conc., ppm*	Pre-Field Audit Conc., ppm	Post-Field Audit Conc., ppm	Percent Change**
K-000264	11.3	9.4	9.3	-1.2
K-001053***	11.6	9.7	8.9	-8.0
K-000913	22.8	19.7	17.8	-9.7
K-009293	32.6	18.4	19.2	4.5
K-009278	41.8	33.8	32.3	-4.5
K-009907***	45.0	34.3	32.1	-6.4
K-000346	54.4	46.6	42.6	-8.7

*Data indicate that the final concentrations reported by Scott Specialty Gases (the target concentrations on the cylinder labels) may have been determined before the initial cylinder incubation period was complete. With one exception (Cylinder K-009293), the post-field audit concentrations were lower than the pre-field audit concentations by one to ten percent. Though these decreases are not statistically significant, based on examination of the average s values, they are indicative of a slower decrease in concentration after the initial incubation period.

**% Change = (post-samp conc - pre-samp conc)/pre-samp conc * 100.

***Cylinders used during field test for dynamic spiking accuracy evaluation.

The IC system was calibrated each day prior to analysis with a series of four calibration standards, bracketing the field sample concentrations, prepared in the impinger reagent and diluted to a representative concentration of reagent. The instrument calibration was repeated at the conclusion of each day's analysis.

To assess the impact of typical analytical interferents present in combustion emissions, a 10 ug/ml chloride solution was spiked with equal concentrations of F^-, Br^-, and $SO_4^=$, and 16.4 ug/ml of NO_3^-. No problems were indicated in quantifying the chloride ion under these conditions.

Ion Exclusion Chromatography --

Carbonate analysis of the midget and Method 5 0.1 N NaOH impinger samples was performed by IEC. The chromatographic system was the same as described for IC analysis with the exception of the column used and the eluent. For the CO_3^{2-} analysis, a Dionex Model 30890 ion exclusion column was employed with deionized water as the eluent at a flow rate of 2 ml/min.

The IEC calibration routine was essentially the same as the IC routine except only three standards were employed. Although the CO_3^{2-} curve is known to be parabolic, a linear curve over a narrow range was employed with CO_3^{2-} standards ranging from 10.7 ug/ml to 42.9 ug/ml.

Data Analysis

The relative error of the HCl CEMS versus the manual method was calculated as shown below. The relative error calculation was based on the assumption that the manual method provides results representative of the emissions from the source and can be correlated to the CEMS data. The individual differences between the HCl flue gas level (dry basis) determined by the manual method and the average flue gas level indicated by the HCl CEMS during the corresponding period were calculated for each run. The arithmetic mean of the differences for a set of runs was then determined. The average HCl flue gas level measured by the manual method for those same runs was determined. Finally, the percent relative error (%RE) of the HCl CEMS was calculated using the following equation:

$$\%RE = \frac{|d|}{RM} \times 100\% \qquad (6)$$

where:

$|d|$ = Absolute value of arithmetic mean difference, ppm_{dv}, and

RM = Average HCl flue gas level for the manual method, ppm_{dv}.

Precisions for the manual method (for HCl and moisture) and the CEMS's were expressed in terms of the standard deviation. For the manual method, the standard deviation was that for the mean of the differences of paired trains as shown.

$$s = \left[\sum_{i=1}^{n} d_i^2/(2n) \right]^{1/2} \qquad (7)$$

where:

d_i = Difference between paired sampling trains, ppm HCl or % H_2O,
n = Number of train pairs, and
s = Standard deviation, ppm HCl or % H_2O.

The precisions for the CEMS's were calculated based on the precision of the manual method and the bias of the CEMS relative to the manual method (see Appendix B for procedure).

An analysis of variance (ANOVA) was used to check the significance of run effects. The run effect was evaluated to show that the flue gas emissions and moisture were fairly consistent from run-to-run during the sampling period. The model for the ANOVA was:

$$Y_{ij} = u_i + R_i + E_{ij} \quad (8)$$

where:

Y_{ij} = The dependent variable, HCl concentration or percent moisture for each run,
u_i = The overall mean for the dependent variable,
R_i = Run "i," i = 1,2,...10, and
E_{ij} = Residual error, j = 1 and 2 for sample A or B in paired-train for run "i."

To determine the bias of the manual method, the HCl concentrations measured following the dynamic spiking in the field were calculated and compared to HCl cylinder concentrations determined by RTI prior to the use of the cylinder in the field. The concentration of the dynamic spike (C_s) was calculated as follows:

$$C_s = \frac{m \times 24.055}{V_{m(std)} \times 36.46} \times 1000 \quad (9)$$

where:

C_s = Concentration of the dynamic spike, ppm_{dv},
m = Mass of HCl in sample, mg,
24.055 = Ideal gas molar volume at 293°K and 760 mm Hg, liters/g-mole,
Vm(std) = Dry gas volume corrected to 293°K and 760 mm Hg, liters, and
36.46 = Mole weight of HCl, mg/mg-mole.

As an expression of bias, the percent recovery of the dynamic spike was calculated as follows:

$$\text{Percent Recovery} = \frac{C_s}{C_t} \times 100\% \quad (10)$$

where:

C_s = Concentration of the dynamic spike, ppm_{dv}, and
C_t = Tag value of the HCl cylinder used for the dynamic spiking, ppm_{dv}.

The significance of flue gas CO_2 removal by the alkaline midget impinger reagent was determined by two methods. The amount of CO_2 removed as a percent of the total gas sample volume was calculated using the following equations:

$$\% \text{ Removed} = \frac{V_{CO2(IC)}}{V_{m(std)} + V_{CO2(IC)}} \times 100\% \quad (11)$$

where:

$V_{co2(IC)}$ = Volume of CO_2 collected in the alkaline impinger reagent determined by IC, liters, and
$V_{m(std)}$ = Dry gas volume corrected to 293°K and 760 mm Hg, liters.

$$V_{co2(IC)} = \frac{m \times 24.055}{61.01} \quad (12)$$

where:

m = Mass of bicarbonate in sample, g,
24.055 = Ideal gas molar volume at 293°K and 760 mm Hg, liters/g-mole, and
61.01 = Mole weight of bicarbonate, g/g-mole.

The second method for expressing the amount CO_2 removed by the alkaline impinger reagent was as a percent collection efficiency (% C.E.) of the total flue gas CO_2 content calculated by the following formula:

$$\% \text{ C.E.} = \frac{V_{co2(IC)}}{\%CO_{2(M3)} \times V_{m(std)}} \times 100\% \quad (13)$$

where:

$\%CO_{2(M3)}$ = The % CO_2 in the flue gas sample determined by Method 3, and
$V_{m(std)}$ = Dry gas volume corrected to 293°K and 760 mm Hg, liters.

For the comparison of the Method 5 trains to the midget impinger trains, Student's t-test was used to determine if the results were different.

SECTION 5

RESULTS AND DISCUSSION

This section presents and discusses the results of all phases of the evaluation of the draft protocol for measurement of HCl emissions. It is divided into four subsections which correspond with those in the section concerning experimental procedures: initial laboratory evaluation, preliminary field test, ruggedness test, and field evaluation test.

LABORATORY EVALUATION

For the first test condition in the laboratory evaluation, HCl was sampled undiluted from a 454 ppm HCl cylinder at a flow rate of 2 liters/minute (lpm) for 20 minutes. The HCl collection efficiency for the first two impingers in each of six sampling trains was calculated. The average collection efficiencies for the first and second acidified impingers are presented in Table 1. They indicate very good collection efficiency for HCl in the acidified impinger reagent at this flow rate and sampling period.

The results for the second and fifth test conditions are also summarized in Table 4. For these two test conditions, a 393 ppm Cl_2 gas was sampled undiluted for 20 minutes from the cylinder at flow rates of 0.5 lpm and 2 lpm, respectively. The Cl_2 collection efficiency was calculated for each impinger in each of the six trains sampling under the two test conditions. The average collection efficiencies shown in Table 4 indicate that more than 98 percent of the Cl_2 passes through the two acidified impingers at a sampling rate of 2 lpm. However, at the lower flow rate of 0.5 lpm, approximately 6 percent is caught by the acidified impingers. Comparing the Cl_2 collected in the first two acidified impingers at the two different flow rates, the absolute amount of Cl^- found was about the same, while the total Cl^- collected in the sampling train at the higher flow rate was four times higher. It is not clear whether an absolute amount of Cl_2 is retained in the first two impingers regardless of flow rate or the higher flow rate (and corresponding reduction in Cl_2 residence time) does reduce the percentage of Cl_2 retained in the first two impingers.

The remaining two test conditions involved sampling mixtures of HCl and Cl_2 at different flow rates. The fourth test condition involved sampling equal proportions of HCl and Cl_2 at a flow rate of 2 lpm for 20 minutes. The purpose of this test condition was to determine if high concentrations of Cl_2 (197 ppm_v) at a high flow rate affected the HCl collection efficiency. The average HCl collection efficiency results are presented in Table 4. They indicate that at a flow rate of 2 lpm, the presence of 197 ppm_v Cl_2 will cause a high bias of about 3% in the measurement of a 221 ppm HCl gas stream.

TABLE 4. COLLECTION EFFICIENCY RESULTS

Impinger	HCl Collection Efficiency (%)*		Cl_2 Collection Efficiency (%)*	
	Test Condition 1 2.0 lpm, 442 ppm HCl	Test Condition 4 2.0 lpm, 221 ppm HCl, 197 ppm Cl_2	Test Condition 5 2.0 lpm, 393 ppm Cl_2	Test Condition 2 0.5 lpm, 393 ppm Cl_2
1 (H_2O, ph = 1)	102.4 ± 3.8	103.0 ± 3.9	0.9 ± 0.1	3.2 ± 0.4
2 (H_2O, ph = 1)	0.4 ± 0.1	3.0 ± 0.4	0.9 ± 0.0	2.9 ± 0.2
3 (0.1 NaOH)	--	--	88.2 ± 2.3	76.0 ± 0.3
4 (0.1 NaOH)	--	--	0.9 ± 0.1	0.2 ± 0.04

*Average of 6 sampling trains ± standard deviation.

Test condition three involved sampling approximately equal levels of HCl and Cl_2 gases (221 and 197 ppm, respectively) at a low flow rate of 0.5 lpm for 20 minutes to determine the effect of HCl on Cl_2 retention in the first two impingers. The results showed a collection efficiency of over 120% for HCl in the first two acidified impingers and a collection efficiency for Cl_2 of 85% and 75% in the two basic impingers indicating that a low flow rate tends to increase the bias caused by the presence of chlorine. These results also suggest that the presence of HCl at a low flow rate does not reduce the retention of Cl_2 in the acidified impingers (i.e., the distribution of Cl_2 in the sampling train at this flow rate remains the same regardless of the presence of HCl).

Based on the results of all the test conditions, there does not appear to be an interaction between HCl and Cl_2 affecting either the HCl collection efficiency or the retention of Cl_2 by the acidified impingers. The sample flow rate appears to affect the distribution of Cl_2 throughout the train with a higher flow rate reducing the amount of Cl_2 retained in the acidified impingers. A higher flow rate does not appear to reduce the HCl collection efficiency at the levels tested. Based on these observations, the acidified midget impinger sampling train, operated at a sampling rate of 2 lpm, appears to minimize the high HCl measurement bias caused by Cl_2 to less than 5% for the conditions tested.

PRELIMINARY FIELD TEST

A summary of all the results for the preliminary field test is presented in Table 5. The table shows the Cl^- content of all field samples as determined by IC, along with the calculated flue gas HCl concentration from each analytical result. The field samples were collected concurrently with operation of an HCl CEMS and the manual sampling results are compared to the HCl concentrations measured by the CEMS averaged over the corresponding sampling period.

The primary objective of the field study was to collect and analyze samples from a MWC to identify any potential problems that might occur with the sampling and/or analytical methods when used at a typical HCl emission source. One potential problem was encountered when the sampling time was extended to one hour and the sampling rate was greater than 2 lpm. Flue gas moisture accumulated in the first impinger and raised the liquid level such that there was physical carry over of the first impinger reagent to the second impinger. This occurred during comparison Runs 2 and 3 and was not observed when the flow rate was maintained close to 2 lpm or when the sampling time was limited to 30 minutes. Based on these observations, an empty water knockout impinger has been added to the recommended sampling train. The potential for Cl_2 absorption in the knockout impinger should be minimal because of the relatively low solubility of Cl_2 in water and, with the knockout impinger design, diffusion of Cl_2 into the water collected in the knockout impinger would be the rate limiting step, and therefore it was not considered necessary to adjust the pH of the condensate.

There were no problems encountered in the IC analysis of the samples despite the relatively low flue gas HCl levels.

TABLE 5. SUMMARY OF PRELIMINARY FIELD TEST RESULTS

Sample ID[a,b]	Chloride Content (mg)	Baghouse Outlet Flue Gas HCl (ppm_v)		Bias: CEM Relative to Manual Method	
	IC	Manual Method	CEMS	ppm_v	Percent
Comparison Samples: 2 lpm for 1 hr					
1-Acid-a	4.93	28.76			
1-Acid-b	<0.01	<0.06			
1-Acid-c	<0.01	<0.06			
1-Acid Total	4.93	28.76	31.5	2.7	9.50%
2-Acid-a	2.02	10.75			
2-Acid-b	0.20	1.041[c]			
2-Acid-c	<0.01	<0.05			
2-Acid Total	2.22	11.79	15.5	3.7	31.43%
3-Acid-a	2.26	11.24			
3-Acid-b	0.26	1.281[c]			
3-Acid-c	<0.01	<0.05			
3-Acid Total	2.52	12.52	16.0	3.5	27.71%
4-Glass-a	3.54	20.96	22.0	1.0	4.92%
4-Glass-b	<0.01	<0.06			
4-Glass-c	<0.01	<0.06			
4-Steel-a	3.46	20.75	22.0	1.2	5.98%
4-Steel-b	<0.01	<0.06			
4-Steel-c	<0.01	<0.06			
6-Glass	1.77	9.15	11.0	1.8	20.20%
6-Steel	1.81	9.67	11.0	1.3	13.71%
Relative Bias				2.2 ± 1.1	
Relative Error Samples: 2 lpm for 30 minutes					
RA-1a	0.39	3.99	4.9	0.9	22.82%
RA-1b	<.01	<0.1			
RA-1c	<.01	<0.1			
RA-2	0.26	2.50	4.8	2.3	91.70%
RA-3	0.31	3.03	4.5	1.5	48.45%
RA-4	0.25	2.51	4.5	2.0	79.29%
RA-5a	0.35	3.48	4.2	0.7	20.69%
RA-5b	<.01	<0.1			
RA-5c	<.01	<0.1			
RA-6	0.19	1.97	4.3	2.3	118.63%
RA-7	0.24	2.48	4.7	2.2	89.25%
RA-8	0.26	2.62	4.7	2.1	79.38%
RA-9a	0.29	2.95	4.6	1.7	56.10%
RA-9b	<.01	<0.1			
RA-9c	<.01	<0.1			
Relative Bias				1.7 ± 0.6	

[a] Run designation and sampling train components: a for 1st impinger, b for 2nd impinger, and c for 3rd impinger.
[b] Data for Run 5-Steel and Run 5-Glass not reported due to leaks in both trains.
[c] Carry over of reagent from 1st to 2nd impinger noticed during sampling.

A second objective of the preliminary field sampling was to determine how well the sampling method responds to changes in effluent concentrations by comparing the sampling results to results determined by an HCl CEMS. A graphic comparison of the flue gas levels measured by the CEMS and the manual method over a three-day period is shown in Figure 7. The manual method and the HCl CEMS both follow the same trends in flue gas HCl levels. Although the flue gas HCl concentration levels changed significantly from the comparison runs to the relative error runs, the relative bias of the CEMS to the manual method calculated from the data in Table 5 remained constant: 2.2 $\pm$ 1.1 ppm for the comparative runs and 1.7 $\pm$ 0.6 ppm for the relative error runs. This indicates an error in the monitor baseline which may be a result of the fact that the HCl gases used to calibrate the HCl CEM were not as low as the flue gas levels.

Using the results for the two paired runs (4 and 6) shown in Table 5, the precision of the manual method can be calculated (0.28 ppm). This precision, along with the bias of the HCl CEMS relative to the manual HCl method for Runs 1-6, can then be used to calculate the precision of the CEMS using the statistical methodology outlined in Appendix B. The calculations yield a precision, expressed as the standard deviation, of 1.1 ppm for the monitor during Runs 1 through 6.

The final objective of the preliminary field sampling was to determine if the use of a stainless steel probe tip as opposed to an all glass sampling probe affects the sampling results. A comparison of the HCl flue gas levels determined using the two probe tips are shown in Table 6. Sampling was conducted at a flow rate of 2 lpm for one hour. (One of the three sampling runs conducted was invalidated due to leaks that developed in both trains.) Based on the limited data, the HCl flue gas levels determined with the two types of probe tips are not significantly different.

TABLE 6. PROBE TIP COMPOSITION COMPARISON: GLASS vs. STEEL

Sampling Run	HCl Concentration (ppm)		Percent Difference*
	Glass Tip	SS Tip	
4-1	21.0	20.1	-1.0
6-1	9.2	9.7	+5.4

*SS relative to glass.

RUGGEDNESS TEST

A summary of the results of the ruggedness test are presented in Table 7. The ruggedness test was designed to test the sensitivity of the sampling method to the variables listed previously in Table 1 (refer to page 14) which were

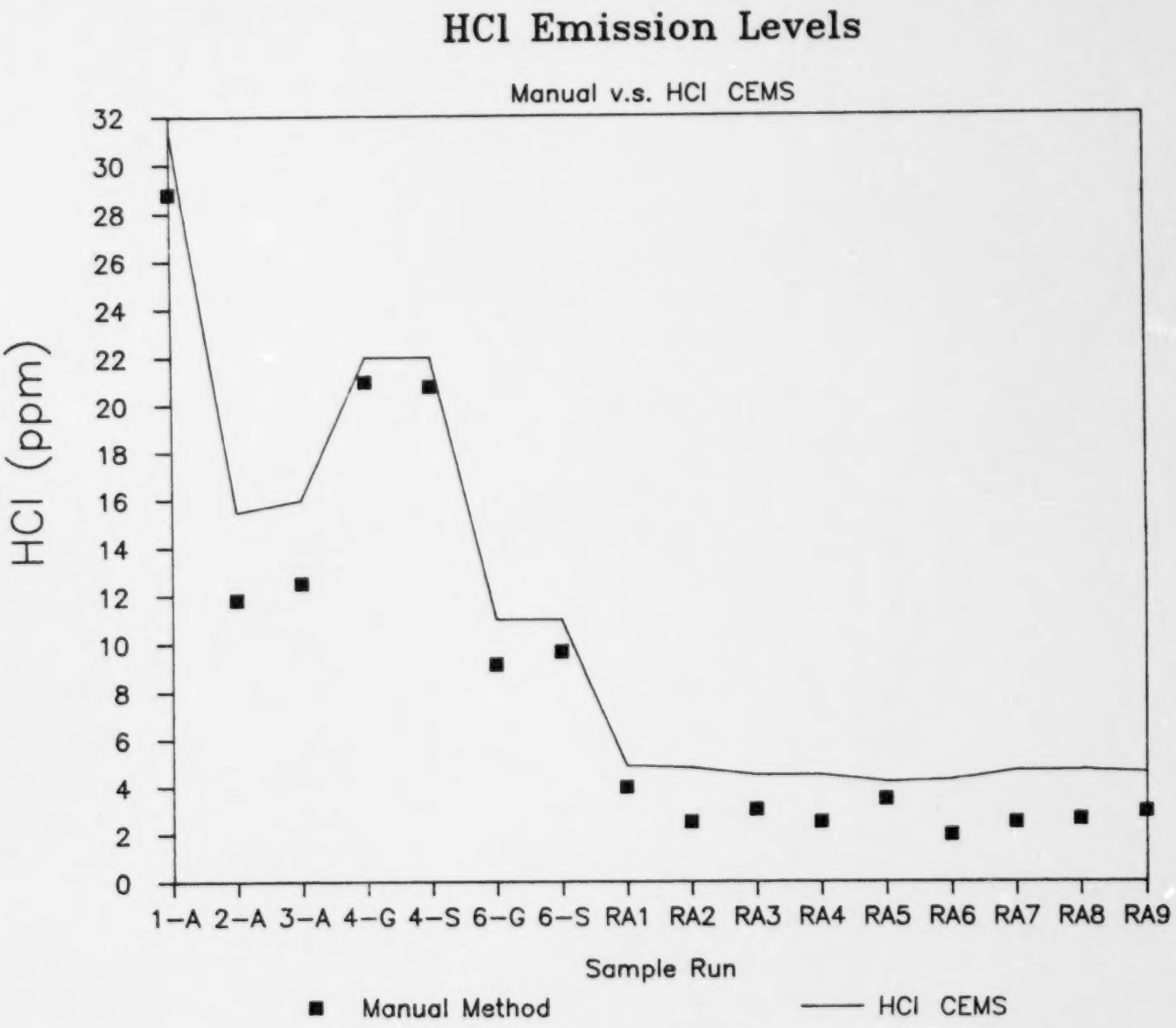

Figure 7. Comparison of trends indicated by the HCl CEMS vs. manual method.

TABLE 7. SUMMARY OF RESULTS FOR RUGGEDNESS TESTING OF HCl SAMPLING METHOD

	Test Run Number							
	1	2	3	4	5	6	7	8
Impinger Train 1	450.5	367.8	423.1	353.5	365.7	419.9	396.3	414.9
Impinger Train 2	443.6	370.9	417.9	358.3	368.3	410.7	389.8	409.3
Average (ppm_v HCl)	447.1	369.4	420.5	355.9	367.0	415.3	393.1	412.1
Range (ppm_v HCl)	6.9	3.1	5.2	4.8	2.6	9.2	6.5	5.6
Average Range (ppm_v HCl)		5.5						
Expected (ppm_v HCl) (Based on 8/31/87 analysis)	494.2	375.3	441.5	378.8	377.0	441.5	421.1	441.5
Percent Recovery	90.5%	98.4%	95.2%	94.0%	97.3%	94.1%	93.3%	93.3%
Average Percent Recovery		94.5%						

Average Results

Average of Variables (% Recovery)

Variable	Optimum Condition	Varied Condition	Difference
Sample Flow Rate (2.0 vs. 2.5 lpm)	94.5%	94.5%	0.0%
Sampling Time (20 vs. 60 minutes)	95.1%	94.0%	1.1%
First Impinger pH (pH 1.0 vs. pH 2.0)	94.1%	94.9%	-0.8%
Impinger Temperature. (ice water vs. 90°F)	93.9%	95.1%	-1.3%
Chlorine Present (0 vs. 50 ppm_v)	93.3%	95.8%	-2.5%
Reagent Volume (15 ml vs. 10 ml)	93.8%	95.3%	-1.5%
Blank	93.0%	96.1%	-3.1%
Standard Deviation			2.5%
Confidence Interval (95% level, 7 degrees of freedom)			2.1%

selected to represent the extreme situations that could be encountered during actual field sampling. A blank variable was also incorporated to determine if the method was in control. The measurement criterion for the ruggedness test was collection efficiency of HCl. The HCl cylinder concentrations determined by independent analysis by Entropy were used to calculate the percent recovery from the Cl^- catch in the acidified impingers.

The blank variable showed a difference of only -3.1%, indicating that the method was in control. The differences for the percent recovery for the six variables at the levels employed is insignificant.

The fact that the blank value, $\pm$ 2.1% (the 95% confidence interval), does not encompass zero suggests that there is a slight bias (approximately 1%) in the data. It should also be noted that sampling HCl with Cl_2 present at 50 ppm as compared to 0 ppm produced an insignificant increase in response. Thus, at Cl_2 concentrations less than 50 ppm, the method can be considered as being insensitive to interference from Cl_2.

FIELD EVALUATION TEST

A matrix of the field samples collected for analysis is presented in Table 8. Much of the sampling and analysis data were reduced on-site to provide an opportunity, if necessary, to modify the test matrix or troubleshoot the HCl-CEMS's. The reduced data were analyzed to: (1) determine the bias and precision of HCl-CEMS's employing the draft HCl method, (2) statistically determine the precision of the draft HCl measurement methodology, (3) estimate the accuracy of the draft HCl method, (4) determine the significance of CO_2 absorbance by the 0.1 N NaOH impinger reagent, and (5) statistically determine if a difference exists between sampling with the draft method and HCl measurement method employing a Method 5 train configuration.

The following subsections describe the results of the field test program and discuss the conclusions made based on the results as they apply to the objectives of the program.

Bias and Precision of HCl Continuous Emission Monitoring Systems

The biases, in terms of the relative error, of the two HCl CEMS's were determined by conducting paired impinger train testing simultaneously with monitor operation on two consecutive days. The results are presented in Table 9. (A third HCl monitor, the MDA Model 7100, was originally included in the test protocol, but the instrument failed to respond to HCl in flue gas samples.) On the first day, the plant was operating the spray dryer (acid gas removal) system normally. On the second day, the plant reduced the lime slurry concentration being fed to the spray dryer, which resulted in an increase in the flue gas concentration of acid gases; these concentrations were, however, still well within the permit limits. The flue gas HCl concentration trends indicated by the two HCl CEMS's and the manual sampling are presented graphically in Figure 8 for the normal acid gas conditions and in Figure 9 for the elevated acid gas conditions.

TABLE 8. TEST SCHEDULE FOR HCl CEMS BIAS FIELD TEST

Test Date	Sample Type	Run No. for Midget Impinger Trains	Run No. for Method 5 Trains	Run No. for Method 3 Samples
Day 1	MI (HCl,CO_2)[1]	1-A	1-C	
	MM5 (HCl,CO_2)[2]	1-B		
	M3 (CO_2)[3]	2-A,		M3-2
	MI (HCl,CO_2,H_2O)[4]	2-B		
	M3 (CO_2)	3-A	3-C	M3-3
	MI (HCl,CO_2, H_2O)	3-B		
	MM5 (HCl,CO_2,)			
Day 2[5]	MI (HCl)[6]	4-A,4-B		
	MI (HCl)	5-A,5-B		
	MI (HCl)	6-A,6-B		
	MI (HCl)	7-A,7-B		
	MI (HCl)	8-A,8-B		
	MI (HCl)	9-A,9-B		
	MI (HCl)	10-A,10-B		
Day 3	MI (HCl,H_2O)[7]	11-A	11-C	
	MM5 (HCl,H_2O)[8]	11-B	11-D	
	MI (HCl,H_2O)	12-A	12-C	
	MM5 (HCl,H_2O)	12-B	12-D	
Day 4	MI (HCl,H_2O)	13-A,13-B[9]		
	MI (HCl,H_2O)	14-A,14-B		
	MI (HCl,H_2O)	15-A,15-B		
	MI (HCl,H_2O)	16-A,16-B		
	MI (HCl,H_2O)	17-A,17-B		
	MI (HCl,H_2O)	18-A,18-B		
	MI (HCl,H_2O)	19-A,19-B		
	MI (HCl,H_2O)	20-A,20-B		
	MI (HCl,H_2O)	21-A,21-B		
	MI (HCl,H_2O)	22-A,22-B		
Day 5	MI (HCl,H_2O)	23-A,23-B[10]		
	MI (HCl,H_2O)	24-A,24-B		
	MI (HCl,H_2O)	25-A,25-B		
	MI (HCl,H_2O)	26-A,26-B		
	MI (HCl,H_2O)	27-A,27-B		
	MI (HCl,H_2O)	28-A,28-B		
	MI (HCl,H_2O)	29-A,29-B		

(continued)

TABLE 8. (continued)

Test Date	Sample Type	Run No. for Midget Impinger Trains	Run No. for Method 5 Trains	Run No. for Method 3
Day 6	MI (HCl)	30-A,30-B		
	MI (HCl)	31-A,31-B		
	MI (HCl)	32-A,32-B		
	MI (HCl)	33-A,33-B		
	MI (HCl)	34-A,34-B		
	MI (HCl)	35-A,35-B		

[1]MI (HCl,CO_2) = U. S. EPA draft method for HCl, with determination of CO_2 absorbed.
[2]MM5 (HCl,CO_2) = Modified U.S. EPA Method 5 for HCl, with determination of CO_2 absorbed.
[3]M3 (CO_2) = U.S EPA Method 3 for carbon dioxide.
[4]MI (HCl,CO_2,H_2O) = Alternative U.S. EPA Method 4 for moisture concurrent with U.S. EPA draft method for HCl.
[5]Dynamic spiking experiments on this day invalidated due to over-pressurized gas delivery manifold.
[6]MI (HCl) = U. S. EPA draft method for HCl only.
[7]MI (HCl,H_2O) = U.S. EPA draft method for HCl, with moisture determination by Alternative Method 4.
[8]MM5 (HCl,H_2O) = Modified U.S. EPA Method 5 for HCl, with moisture determination by Method 4.
[9]Run 13 was originally invalidated due to failed posttest leak check on impinger train B, and Run 22 was added; but based on moisture results, data were considered valid.
[10]Run 23 was invalidated due to failure to maintain proportional sampling rate, and Run 29 was added.

TABLE 9. SUMMARY OF HCl CEMS AND MANUAL SAMPLING RESULTS

Run	TECO Model 15/200		Bran & Luebbe Ecometer		HCl Manual Sampling		Bias: CEM Relative to Manual Sampling	
	HCl		HCl		HCl[a]	Moisture[a]	TECO	B&L
	(ppm_w)	(ppm_d)	(ppm_w)	(ppm_d)	(ppm_d)	(%)	(ppm_d)	(ppm_d)
Normal Acid Gas Levels								
13	3.5	4.3	1.8	2.2	4.1	19.9	0.2	-1.9
14	3.5	4.4	1.2	1.5	3.0	19.6	1.4	-1.5
15	4.6	5.6	1.7	2.0	5.4	18.6	0.2	-3.4
16	3.6	4.4	1.0	1.1	3.5	17.3	0.9	-2.4
17	3.0	3.6	0.6	0.7	2.6	18.0	1.0	-1.9
18	2.3	2.9	0.5	0.6	3.3	19.4	-0.4	-2.7
19	1.9	2.3	0.6	0.7	2.9	19.5	-0.6	-2.2
20	2.1	2.5	0.4	0.4	3.3	17.0	-0.8	-2.9
21	4.9	6.0	1.6	2.0	6.6	18.3	-0.6	-4.6
22	2.7	3.3	0.7	0.8	3.9	19.3	-0.6	-3.1
Mean	3.2	3.9	1.0	1.2	3.9	18.7	0.07 ± 0.79[b]	-2.7 ± 0.90[b]
Relative Error:[c]							1.6%	68.6%
Elevated Acid Gas Levels								
24	7.5	9.3	3.2	4.0	9.5	19.1	-0.2	-5.5
25	7.9	9.9	3.1	3.9	10.5	20.3	-0.6	-6.6
26	15.2	18.8	8.9	11.0	20.0	19.3	-1.2	-9.0
27	10.4	12.6	3.1	3.7	10.7	17.8	1.9	-7.0
28	6.8	8.3	1.8	2.2	5.5	18.7	2.8	-3.3
29	3.7	4.7	0.4	0.5	3.3	20.9	1.4	-2.8
Mean	8.6	10.6	3.4	4.2	9.9	19.4	0.68 ± 1.58[b]	-5.7 ± 2.35[b]
Relative Error:[c]							6.8%	57.6%

[a]Average of paired trains.

[b]Mean Difference = (Monitor Response - Manual Measurement)/Number of Runs.

[c]Relative Error = Mean Difference / Average Manual Measurement.

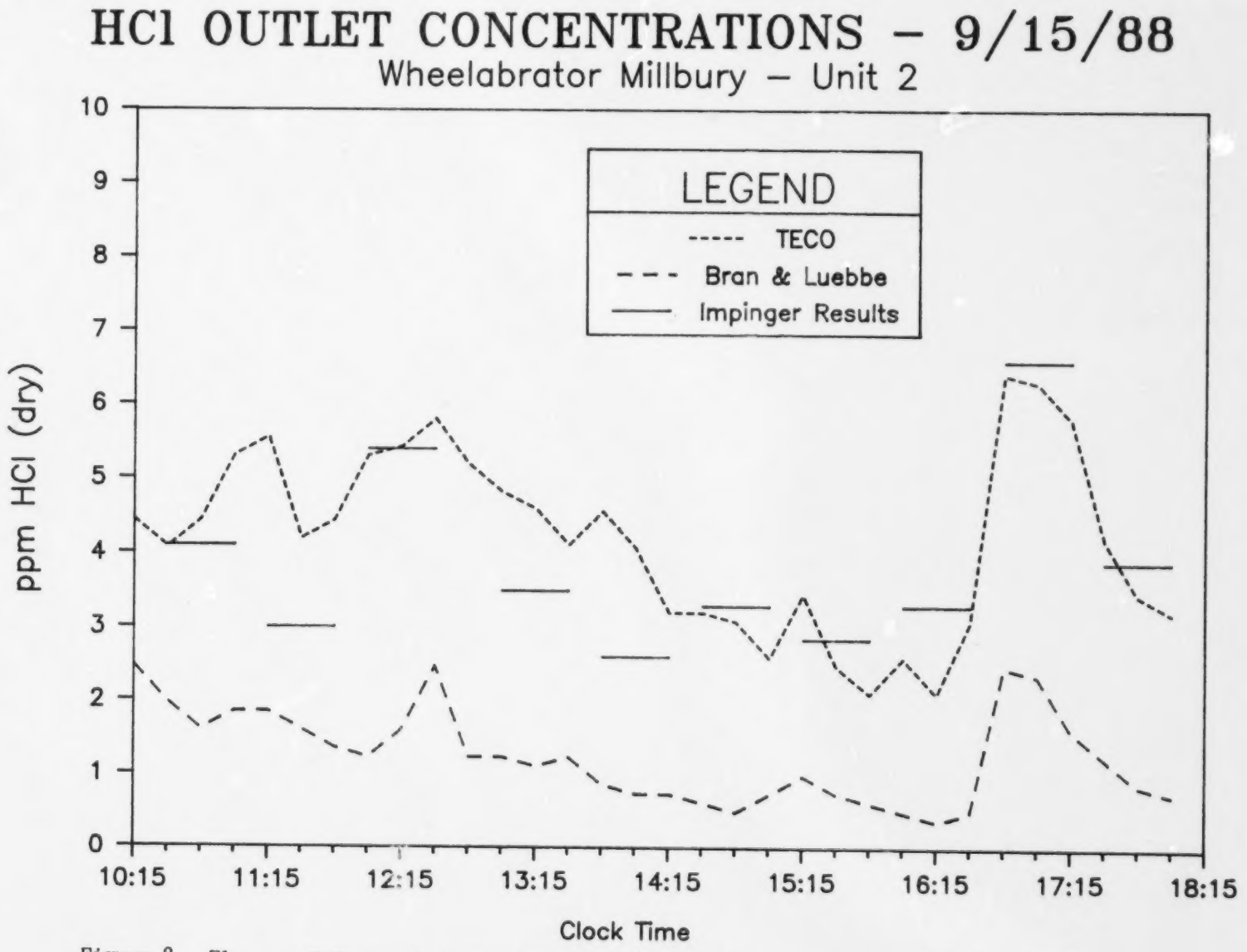

Figure 8. Flue gas HCl trends indicated by HCl CEMS's under normal acid gas conditions.

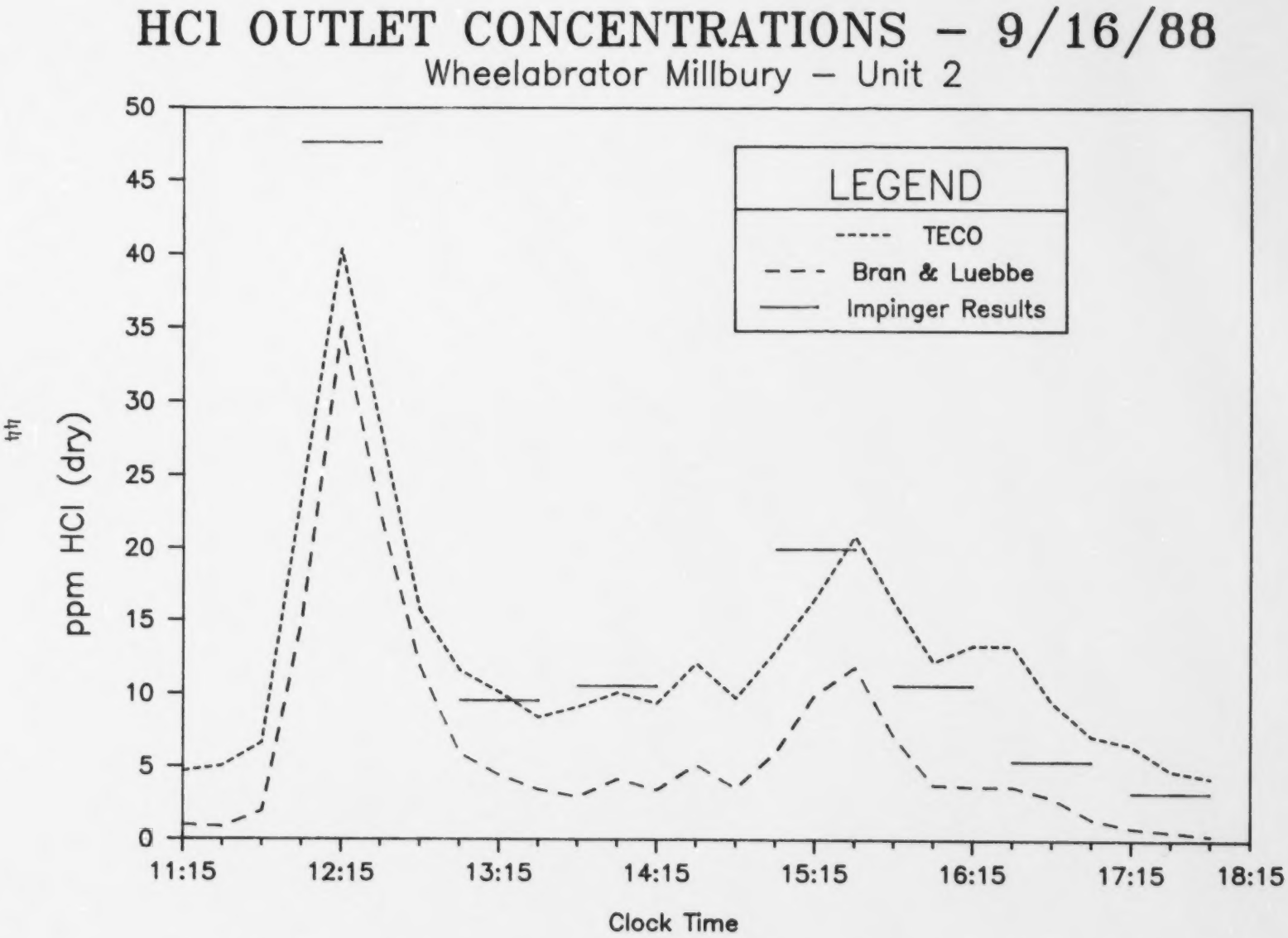

Figure 9. Flue gas HCl trends indicated by HCl CEMS's under elevated acid gas conditions.

The relative error of the TECO system, for the 10 runs at the normal flue gas levels, was 1.6% at an average flue gas HCl concentration of 3.9 ppm. During the elevated acid gas conditions, the relative error of the TECO system was 6.8% at an average flue gas HCl concentration of 9.9 ppm. As shown in Figure 9, the flue gas HCl levels fluctuated considerably during the elevated acid gas condition. Fluctuating levels of a pollutant during this type of testing are not desirable.

The relative error results for the Braun and Luebbe system were not as good as the TECO, with a relative error of 68.6% for the normal acid gas condition and 57.6% for the elevated acid gas condition. As discussed earlier, the Braun and Luebbe system employed an internal liquid standard for calibration and was not calibrated with the HCl cylinder gases. Examination of Figures 8 and 9 both indicate that the Braun and Luebbe system was following the changes in flue gas HCl levels indicated by the TECO HCl CEMS and the manual method. The Braun and Luebbe appears to have potential for accurately measuring the HCl levels encountered during this test program, provided an accurate calibration approach can be developed using HCl cylinder gases.

Using the precision data for the manual method shown in Table 10, the CEM bias data in Table 9, and the statistical procedure presented in Appendix B, the precision of the TECO and Bran and Luebbe monitors can be calculated. For example, during Runs 13 through 22 at normal HCl levels, the precision of the TECO monitor was 0.75 ppm and the bias, 0.07 ppm, was not statistically significant in comparison. In Runs 24 through 29, the elevated acid gas levels produced a real increase in the variability of the data with a precision (standard deviation) for the TECO equal to 1.5 ppm. However, the increase in the bias to 0.68 ppm was not significant.

The Bran and Luebbe monitor bias for Runs 13 through 22 was 2.66 $\pm$ 0.87, which was statistically significant. The standard deviation of 0.87 was lower than might have been expected. The Bran and Luebbe bias for Runs 24 through 29 was 5.7 $\pm$ 2.3 ppm; with the higher acid gas concentrations came increased bias and data variability. These precision data provide useful information on the performance of the two monitors under different operating conditions.

Results of Paired Midget Impinger Train Sampling

Table 10 presents the HCl flue gas concentations determined employing paired midget impinger trains using the draft HCl method. The precision of the manual method expressed as the standard deviation of the paired train differences was determined for the sets of runs during normal operation and during elevated acid gas conditions. The precision, in terms of the standard deviation for the difference of paired trains, for Runs 13 through 22 was 0.24 ppm and Runs 23 through 29 was 0.49 ppm. These standard deviations are more representative of the method precision than the standard deviation of any particular run. The precision of the method under normal operating conditions, 0.24 ppm, is in good agreement with the earlier value of 0.28 ppm calculated from results of the preliminary field testing (see Table 5) obtained under similar operating conditions. The precision expressed as the relative standard deviation was 6.2% and 3.2%, respectively, at the two HCl concentration levels.

TABLE 10. SUMMARY OF PAIRED MIDGET IMPINGER TRAIN RESULTS

Run	Train A		Train B		Difference	
	HCl (ppm)	H_2O	HCl (ppm)	H_2O	HCl (ppm)	H_2O
Flue Gas Samples Collected during Normal Plant Operation						
13	3.9	19.3%	4.3	20.4%	-0.4	-1.0%
14	2.9	20.3%	3.1	18.8%	-0.2	1.5%
15	5.3	18.7%	5.5	18.4%	-0.2	0.3%
16	3.2	18.2%	3.7	16.4%	-0.5	1.8%
17	2.7	18.0%	2.5	18.0%	0.2	0.0%
18	3.4	19.3%	3.2	19.5%	0.2	-0.2%
19	2.7	19.5%	3.0	19.4%	-0.3	0.1%
20	3.4	17.6%	3.1	16.3%	0.3	1.3%
21	6.3	18.0%	6.8	18.5%	-0.5	-0.5%
22	4.1	18.1%	3.7	20.5%	0.4	-2.4%
Mean	3.8	18.7%	3.9	18.6%	-0.1 ± 0.24[a]	$0.09\% \pm 0.84\%$[a]
Flue Gas Samples Collected during Elevated Acid Gas Condition						
23	47.2	21.0%	48.7	21.2%	-1.5	-0.2%
24	9.4	19.2%	9.5	19.0%	-0.1	0.2%
25	10.4	20.1%	10.6	20.5%	-0.2	-0.4%
26	20.4	19.7%	19.6	18.9%	0.8	0.8%
27	10.8	18.7%	10.5	16.9%	0.3	1.8%
28	5.2	19.0%	5.7	18.4%	-0.5	0.6%
29	3.4	20.3%	3.2	21.5%	0.2	-1.2%
Mean	15.1	19.7%	15.4	19.5%	0.14 ± 0.49[a]	$0.23\% \pm 0.63\%$[a]

[a]Precision of method is standard deviation for paired trains (see Equation 7, page 29) expressed in ppm for HCl and % for moisture.

The precision of the midget impinger sampling method for moisture determination (necessary to correct wet HCl CEMS results to a dry basis) was also determined. During the first day of paired train testing, the precision in terms of the standard deviation for the moisture determination was 0.84% and, for the second day of paired train testing, the precision was 0.63%.

As seen in Figures 8 and 9, the manual method results follow the trends indicated by the HCl CEMS for changes in the flue gas HCl concentration.

The knockout plus the first impingers and the second impinger were recovered and analyzed separately to determine the HCl collection efficiency of the train. In no case was the Cl^- content of the second impinger more than 1% of the total Cl^- content of the train. This result confirms the earlier results of the laboratory work that under these sampling conditions the HCl collection is essentially 100%. In most cases, the Cl^- concentration of the second impinger was less than the limit of quantification (estimated to be < 0.5 ug/ml).

Results for On-site Dynamic Spiking of the Midget Impinger Sampling System

The results of the dynamic spiking of the midget impinger sampling system are presented in Table 11 along with the gas cylinder values determined independently by RTI. The bias of the HCl sampling and analytical methodology was 7.1% and 5.5% for HCl gas concentrations of 9.7 ppm and 34.3 ppm, respectively. Considering the reactive nature of HCl and the inherent problems that this reactivity causes in obtaining accurate data, a bias of only +6 to +7% suggests that the method is performing well.

TABLE 11. SUMMARY OF DYNAMIC SPIKING RESULTS

Run Nos.	Cylinder Number	Average HCl Gas Concentration		Bias
		Independent Gas Cylinder Value (ppm)	Cylinder Value Determined On-site (ppm)	
30,31,32	K-1053	9.7[a]	10.4[b]	+ 7.1%
33,34,35	K-9907	34.3[c]	36.2[b]	+ 5.5%

[a] Average result for a sampling run with triplicate impinger trains and a sampling run with duplicate impinger trains.
[b] Average result for three sampling runs, each with duplicate impinger trains.
[c] Average result for three sampling runs, each with triplicate impinger trains.

Carbon Dioxide Absorption by 0.1 N NaOH Impinger Reagent

The results of the test runs conducted to determine the absorption of CO_2 by the 0.1 N NaOH impinger reagent are presented in Table 12. One impinger containing NaOH was used in each sampling train.

TABLE 12. FLUE GAS CO_2 REMOVAL AND COLLECTION EFFICIENCY (CE) BY 0.1 N NaOH REAGENT

		Midget Impinger Train				Method 5 Train	
		Train A		Train B		Train C	
Run	% CO_2	Removed	CE	Removed	CE	Removed	CE
1	----	0.03%	-----	0.03%	-----	0.01%	-----
2	9.5	0.04%	0.005%	----	-----	----	-----
3	10.0	0.03%	0.003%	0.01%	0.001%	0.02%	0.002%
Average	9.8	0.03%	0.004%	0.02%	0.001%	0.02%	0.002%

The amount of CO_2 removed from the flue gas sample by the midget impingers and the Method 5-type impingers containing the 0.1 N NaOH reagent was insignificant relative to the total gas sample. For the midget impingers at a sampling rate of 2 liters/minute, the CO_2 removal averaged less than 0.03% of the gas sample volume, and accordingly had a CO_2 collection efficiency averaging less than 0.004%. For the Method 5-type impinger at a sampling rate of less than 10 liters/minute, the CO_2 removal and CO_2 collection efficiency averaged less than 0.02% and 0.002%, respectively. The results indicate that a 0.1 N NaOH impinger reagent has little effect on the measured gas sample volume due to CO_2 removal.

Comparison of Midget Impinger Train to Method 5-Type Train for HCl Sampling

The results of the mixed quad-train sampling comparing the midget impinger train to a Method 5 train with 0.1 N NaOH for HCl collection are presented in Table 13.

Although unintended, the first sampling run was conducted during a period of relatively high HCl flue gas levels. The results for Run 11, conducted at the elevated flue gas level, for the two sampling methodologies were in good agreement, and the elevated HCl level was also reflected by the TECO HCl CEMS. Based on a paired t-test, the results obtained by the two manual sampling methodologies were not significantly different.

TABLE 13. RESULTS OF THE MIXED QUAD-TRAIN SAMPLING FOR HCl

Run	HCl Flue Gas Concentration (ppm)				
	Midget Impinger Train		Method 5 Impinger Train		TECO HCl CEMS
	Train A	Train B	Train C	Train D	
11	21.6	20.8	22.6	19.8	16.3
12	5.2	4.6	2.8	2.5	4.8

During Run 12, the flue gas HCl levels had returned to normal. The results obtained with the Method 5 sampling train were significantly lower than those obtained with the midget impinger sampling train. The TECO HCl CEMS results agreed with the midget impinger train results.

The difference seen between the two sampling trains was investigated. As with the midget impinger trains, the first and second impingers from each Method 5 train were recovered and analyzed separately. The Cl^- concentrations in the second impinger of each Method 5 train were below the limit of quantification, indicating that the HCl collection efficiency of the Method 5 train was acceptable. The reason for the low bias seen for the Method 5 train for Run 12 must have been caused by a loss of HCl prior to the impingers. One possible explanation could be removal of the HCl by unreacted lime from the spray dryer system collecting on the filter of the Method 5 train. More unreacted lime may have been present during Run 12 when the flue gas HCl level was low than during Run 12 when the HCl level was higher. The presence of unreacted lime on a Method 5 filter has been shown to cause a negative bias in HCl measurements.[15]

Additionally, gaseous HCl can be lost from the sample stream both due to reaction with glass surfaces and with alkaline particulate material such as lime.[16,17] It has also been shown in the referenced works that shorter sampling times result in greater relative errors. Thus, a 1-hour or greater sampling time is recommended.

The references also indicate that the common practice of inserting a glass wool plug in the probe tip to remove particulate matter from the sample gas stream can greatly increase the loss of gaseous HCl relative to other filtering procedures. The use of a probe with the nozzle opening opposite instead of perpendicular to the gas flow has been shown to substantially reduce the amount of particulate matter collected. This procedure, in combination with use of a Teflon filter as described in the present work, should minimize the collection of particulate matter.[18] Therefore, it has been included in the draft method presented in Appendix A.

ANOVA for Run Effects

For the ten-run paired train sampling during normal flue gas conditions, the run effect calculated using the ANOVA was not significant at the 95% confidence level with a probability (P) equal to 0.1. Similarly the run effect for the moisture results was not significant (P = 0.1).

For the seven-run paired train samples, the run effect for HCl was found to be significant, (P = 0.009). However, an F test was run on the seven-run HCl results to check for equal variance between the paired trains, and the variances were found to equal (P = 0.95). The run effect for the moisture results was not significant (P = 0.25).

SECTION 6

QUALITY ASSURANCE AND QUALITY CONTROL

This section discusses the quality assurance and quality control (QA/QC) procedures implemented for the laboratory and field test evaluations of the HCl metals sampling and analytical protocol. QA/QC procedures are necessary to document and quantify the acceptability and reliability of the data generated and are particularly important for method development programs which rely on nonroutine measurements. The QA/QC guidelines and procedures were outlined in the QA/QC plans for the field and laboratory evaluations and emphasized the following areas: data quality objectives, adherence to prescribed sampling and analytical procedures, data recording, sample custody, and calibration procedures. The QA/QC activities and results are described in the following sections.

SAMPLING QA/QC ACTIVITITES

Quality control for the flue gas sampling for the field evaluation testing emphasized: (1) equipment calibration, (2) glassware and sampling equipment cleaning, (3) procedural quality control checks, and (4) sample custody procedures. Key activities and quality control results for each of these areas are discussed below.

Pretest calibrations as specified by EPA Methods 6, 5, 4, 3, and 2 were conducted on pitot tubes, sampling nozzles, manometers/differential pressure gauges, temperature sensors, analytical balances, and Orsat analyzers (see Table 14). Both pre- and posttest calibrations were also performed on the dry gas meters used for the sampling. Calibration procedures followed the "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Source Specific Methods."[19] All the equipment mentioned above met the calibration criteria specified in the applicable Method. Differences between pre- and posttest dry gas meter calibrations for each run were less than 2 percent.

For the field test evaluation, reagent blanks were collected prior to and during the field test program. The reagent blanks collected prior to the test were stored in precleaned sample jars and analyzed prior to the test; these included 0.1 N sulfuric acid absorbing solution and 0.1 sodium hydroxide absorbing solution. Reagent blanks collected during the field evaluation were analyzed with the field samples. The analysis of these samples showed Cl^- levels below the detection limit, indicating little or no contamination in the reagents and precleaned glassware.

TABLE 14. EQUIPMENT REQUIRING PRETEST CALIBRATION

Parameter	Method	Calibrated Equipment Used to Measure Parameters						
		Type S Pitot Tube	Manometer	Temperature Measuring Device	Orsat	Nozzles	Balances	Dry Gas Meter
Volumetric Flue Gas Flow Rate	EPA Method 2	X	X	X	---	---	---	---
Gas Phase Composition								
Moisture	EPA Method 4	X	X	X	---	---	X	X
Molecular Weight	EPA Method 3	---	---	---	X	---	---	---
HCl	EPA Method 5 - modified	X	X	X	X	X	---	X
HCl	EPA Method 6 - modified	---	X	X	X	---	---	X

The following quality control checks were conducted for HCl sampling; where applicable, results of these checks are noted.

- All sampling equipment used was thoroughly checked to ensure that it had clean and operable components and had not been damaged in shipment.
- The oil manometer or magnehelic gauge used to measure pressure across the S-type pitot tube was leveled and zeroed.
- Each sampling train was visually inspected for proper assembly before use.
- Sampling ports were sealed to help prevent possible air inleakage.
- All sampling data and calculations were recorded on preformatted data sheets.
- Any unusual occurrences were noted during each run on the appropriate data form.

In addition to the general QC procedures listed above, the following method-specific QC procedures were also incorporated into the sampling scheme.

Volumetric Flow Rate Determination

- The S-type pitot tube was visually inspected before and after sampling; no damage was found.
- The roll and pitch axes of the S-type pitot tube and sampling nozzle were properly maintained.

Moisture Determination

- A weighed charge of silica gel or Drierite was added to the final impinger prior to the test and was quantitatively recovered after the test and the weight determined (within 0.1 g).
- Each impinger was weighed to the nearest 0.1 gram before and after sampling.
- Ice was maintained in the ice bath during each run.

Molecular Weight Determination

- The Orsat analyzer was leak-checked before and after each run; no leaks were indicated.
- A constant sampling rate (10 percent) was used in withdrawing a sample.

- The Orsat analyzer was leveled and the fluid levels zeroed prior to use.

- The Orsat analyzer was purged prior to sample collection.

- Orsat solutions were changed when more than six passes were required to obtain a stable reading for any component.

HCl Train Sampling

- Preliminary velocity, temperature, and moisture was determined to aid in conducting isokinetic sampling.

- The proper sampling nozzle size was determined for the Method 5 train.

- Sampling trains were assembled in an environment free from uncontrolled dust.

- Known volumes (within 1.0 ml) of the proper reagent were charged to each reagent-containing impingers prior to the test and the final volume of the contents of each impinger were determined to the nearest 1.0 ml after the test.

- The sampling nozzle was visually inspected before and after each test run; broken nozzles were discarded.

- The entire sampling train was leak-checked before and after each test run; results are discussed below.

- Ice was maintained in the ice bath.

- The probes and filters were maintained at 120° $\pm$14°C.
- Readings of the dry gas meter, pressures, temperatures, and pump vacuum were recorded at regular intervals during sampling. Isokinetic sampling velocity was maintained within $\pm$10 percent of the duct velocity.

- The probe, filter, and impingers were immediately recapped as the train was disassembled.

SAMPLE CUSTODY, TRANSPORTATION PRECAUTIONS, AND SAMPLE STORAGE

Sample custody procedures for the field evaluations were based on EPA recommended procedures. Since field samples were analyzed on-site, the custody procedures emphasized careful documentation of sample collection and field analytical data.

All sampling data, including information regarding sampling times, locations, and any specific considerations associated wtih sample acquisition were recorded in black ink on preformatted data sheets. Following sample

collection, all samples were given a unique alphanumeric sample identification code. Sample labels were completed and affixed to each sample container. The sample volumes were determined and recorded, and the liquid levels were marked on each bottle.

ANALYTICAL QA/QC ACTIVITIES

All analyses for both test programs were performed using accepted laboratory procedures in accordance with the specified analytical protocols. The specific quality control procedures for sample preparatory work and for sample analyses by IC are discussed below.

Analytical quality control included analysis of a laboratory blank, method spikes, and duplicates. The laboratory blank consisted of the DI H_2O used for any sample dilutions being analyzed following the procedures specified in the draft EPA method to check for laboratory contamination. Method spikes for the midget impinger train were prepared by spiking a representative amount of HCl into 30 ml of 0.1 N H_2SO_4 and adjusting the volume to 100 ml using DI H_2O. Similarly, method blanks were prepared for each type of Method 5 impinger train reagent. The method spikes were handled and analyzed in the same manner as the field samples.

The QC criteria followed for the IC analysis of HCl samples were:

- The response for replicate injections of reagent blanks and field samples had to be within 5% of their mean. Samples were injected until the 5% criterion was met or corrective action was taken.

- The maximum deviation for the response to each calibration standard analyzed before and after field samples from the mean of the calibration standard response was 5%. If this value was exceeded, the instrument was exhibiting unacceptable drift, the field sample analysis was not valid, and corrective action was taken.

Audits of the sample preparation and analysis procedures were conducted using an NBS Cl^- standard prepared in sampling reagent and handled in a manner similar to actual samples (i.e., sample voluming and dilution). The NBS standard was also prepared for an audit of the analytical system alone.

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APPENDIX A.

DRAFT METHOD FOR

THE DETERMINATION OF HCl EMISSIONS

FROM MUNICIPAL AND HAZARDOUS WASTE INCINERATORS

This method has been drafted based on the results of laboratory and field studies carried out under contract to the Source Branch of the Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory (QAD/AREAL), United States Environmental Protection Agency (U.S. EPA). The method is still under investigation and is subject to revision.

U. S. Environmental Protection Agency
Quality Assurance Division
Research Triangle Park, North Carolina 27711

April 1989

THE DETERMINATION OF HCl EMISSIONS
FROM MUNICIPAL AND HAZARDOUS WASTE INCINERATORS

1. Applicability, Principle, Interferences, Precision, Bias, and Stability

1.1 Applicability. The method is applicable to the determination of hydrogen chloride (HCl) emissions from municipal and hazardous waste incinerators.

1.2 Principle. An integrated gas sample is extracted from the stack and passed through acidified water. In the acidified water, the HCl gas is solubilized and forms chloride (Cl^-) ions. Ion chromatography (IC) is used for Cl^- analysis.

1.3 Interferences. Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences. One likely interferant is diatomic chlorine (Cl_2) gas which disproportionates to HCl and hypochlorous acid (HOCl) upon dissolution in water. Cl_2 gas exhibits a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present. Sampling a 400 ppm HCl gas stream containing 50 ppm Cl_2 with this method does not cause a significant bias. Sampling a 220 ppm HCl gas stream containing 180 ppm Cl_2 results in a positive bias of 3.4% in the HCl measurement.

1.4 Precision and Bias. The within laboratory relative standard deviation is 6.2% and 3.2% at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not exhibit any bias when sampling Cl_2 concentrations less than 50 ppm.

1.5 Stability. The collected samples can be stored for up to 4 weeks prior to analysis.

1.6 Lower Detection Limit. The lower detection limit of the analytical method is 0.1 ug/ml of sample solution.

2. Apparatus

2.1 Sampling. The sampling train is shown in Figure A-1, and component parts are discussed below.

2.1.1 Probe. Borosilicate glass, approximately 3/8-in. (9-mm) inside diameter, with a heating system to prevent condensation. A 3/8-in. (9-mm) inside diameter Teflon elbow should be attached to the inlet of the probe and a 1-in. (25-mm) length of Teflon tubing with a 3/8-in. (9-mm) inside diameter should be attached at the open end of the elbow to permit the opening of the probe to be turned away from the gas stream, thus reducing the amount of particulate entering the train. This probe configuration should be used when the concentration of particulate matter in the emissions is high. When high concentrations of particulate matter are not present, the Teflon elbow is not

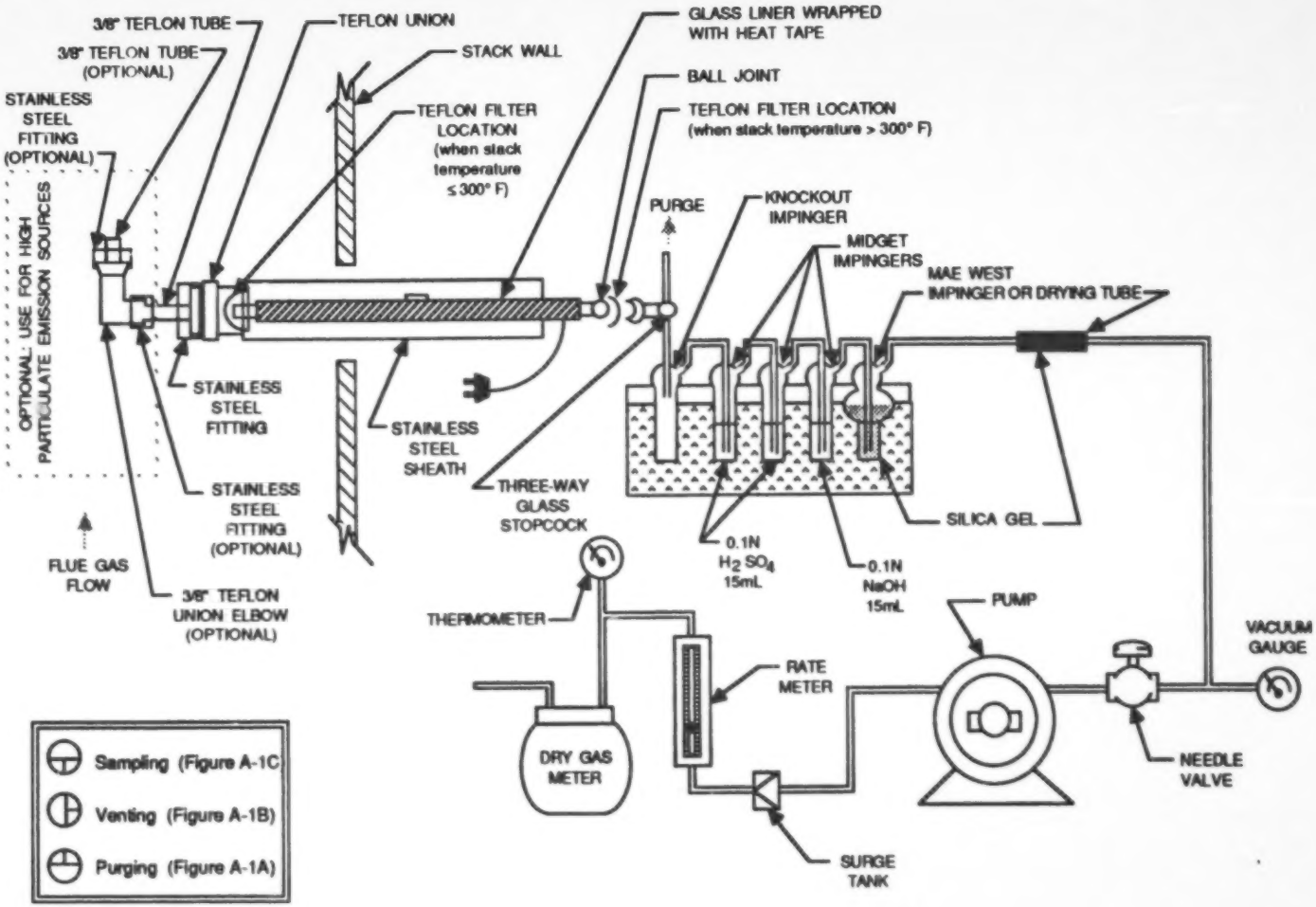

Figure A-1. HCl sampling train.

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necessary, and the probe inlet can be perpendicular to the gas stream. A glass wool plug should not be used to remove particulate matter; use of such a filter device will most likely result in a negative bias in the data.[1] Instead, a Teflon filter (see Section 2.1.5) should be installed at the inlet (for stack temperatures ≤300°F) or outlet (for stack temperatures >300°F) of the probe.

2.1.2 Three-way Stopcock. A borosilicate, three-way glass stopcock with a heating system to prevent condensation. The heated stopcock should connect directly to the outlet of the probe and the inlet of the first impinger. The heating system should be capable of preventing condensation up to the inlet of the first impinger. Silicone grease may be used, if necessary, to prevent leakage.

2.1.3 Impingers. Four 30-ml midget impingers with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. For sampling at high moisture sources or for extended sampling times greater than one hour, a midget impinger with a shortened stem (such that the gas sample does not bubble through the collected condensate) should be used in front of the first impinger.

2.1.4 Drying Tube or Impinger. Tube or impinger, of Mae West design, filled with 6- to 16-mesh indicating type silica gel, or equivalent, to dry the gas sample and to protect the dry gas meter and pump. If the silica gel has been used previously, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

2.1.5 Filter. 25-mm Teflon with 1.0-um pore size, Schleicher and Schuell® 41-01510 or equivalent. A lower porosity filter may be necessary at some sources to prevent chloride-containing particulate matter from penetrating the filter. Locate between probe liner and Teflon elbow at stack temperatures 300°F or less and at outlet of probe liner at stack temperatures greater than 300°F.

2.1.6 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease may be used, if necessary.

2.1.7 Sample Line. Leak-free, with compatible fittings to connect the last impinger to the needle valve.

2.1.8 Valve. Needle valve, to regulate sample gas flow rate.

2.1.9 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through train. Install a small surge tank between the pump and the rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

2.1.10 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of selected flow rate of 2 liters/min.

2.1.11 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate and conditions encountered during sampling, and equipped with a temperature gauge

(dial thermometer or equivalent) capable of measuring temperature to within 3°C (5.4°F).

2.1.12 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for the elevation differences between the weather station and sampling point shall be applied at rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.13 Vacuum Gauge. At least 760 mm Hg (30 in. Hg) gauge to be used for leak check of the sampling train.

2.1.14 Purge Pump, Purge Line, Drying Tube, Needle Valve, and Rate Meter. Pump capable of purging sample probe at 2 liters/min, with drying tube, filled with silica gel or equivalent, to protect pump, and a rate meter, 0 to 5 liters/min.

2.2 Sample Recovery.

2.2.1 Wash Bottles. Polyethylene or glass, 500 ml or larger, two.

2.2.2 Storage Bottles. Glass, with Teflon-lined lids, 100 ml, to store impinger samples (two per sampling run). During clean-up, the two front (acidified) impinger contents should be combined. The 0.1 N NaOH solutions contained in the two rear impingers can be discarded, as these solutions are included only to absorb Cl_2, which, if present, could damage the sample pump.

2.3 Sample Preparation and Analysis. The materials required for volumetric dilution and for chromatographic analysis of impinger samples are described below. The ion chromatograph (IC) used may be configured for suppressed or non-suppressed ion chromatography.

2.3.1 Volumetric Flasks. Class A, 100-ml size.

2.3.2 Volumetric Pipettes. Class A, assortment, to dilute samples to calibration range of the IC.

2.3.3 Ion Chromatograph. Suppressed or non-suppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, a strip chart recorder, and peak heights may be used provided the 5 percent repeatability criteria for sample analysis and the linearity criteria for the calibration curve can be met.

3. Reagents

Unless otherwise indicated, all reagents should conform, as a minimum requirement, to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade) or, when

materials of this grade are unavailable, the reagents used should be the best available grade.

3.1 Sampling.

3.1.1 Water. Deionized and distilled that conforms to ASTM Specification D 1193-77, Type 3.

3.1.2 0.1 N Sulfuric Acid. To prepare 100 mL of the absorbing solution for the front impinger pair, slowly add 0.28 mL of sulfuric acid to about 90 mL of water while stirring, and adjust the final volume to 100 mL using additional water. Shake well to mix the solution.

3.1.3 0.1 N Sodium Hydroxide. To prepare 100 mL of the absorbing solution for the back pair of impingers, dissolve 0.40 g of solid sodium hydroxide in about 90 mL of water and adjust the final solution volume to 100 mL using additional water. Shake well to mix the solution.

3.2 Sample Preparation and Analysis.

3.2.1 Water. Same as Section 3.1.1.

3.2.2 Blank Solution. A separate blank solution of acidified reagent should be prepared for analysis with the field samples. Dilute 30 ml of acidified reagent to 100 ml with water in a separate volumetric flask.

3.2.3 NaCl Stock Standard Solution. Solutions containing a nominal certified concentration of 1000 mg/L are commercially available as convenient stock solutions from which working standards can be made by appropriate volumetric-dilution. Alternately, concentrated stock solutions may be produced from reagent grade sodium chloride that has been dried at 110°C for 2 hours or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. The exact Cl^- concentration can be calculated using the expression:

$$\text{ug } Cl^- / \text{ mL} = \text{g of NaCl} \times 10^3 \times 35.453/58.44$$

Refrigerate the stock standard solutions and store no longer than one month.

3.2.4 Chromatographic Eluent. Effective eluents for non-suppressed ion chromatography using a resin- or silica-based weak ion exchange column are a 4 mM potassium hydrogen phthalate solution, adjusted to a pH of 4.0 using a saturated sodium borate solution, and a 4 mM 4-hydroxy benzoate solution, adjusted to a pH of 8.6 using 1 N sodium hydroxide. An effective eluent for suppressed ion chromatography is a solution containing 3 mM sodium bicarbonate and 2.4 mM sodium carbonate. Other dilute solutions buffered to a similar pH that contain no ions interfering with the chromatographic analysis may be used. If, using suppressed ion chromatography, the "water dip" resulting from sample injection is interfering with the chloride peak, use a 2 mM sodium hydroxide/2.4 mM sodium bicarbonate eluent.

3.2.5 Quality Control Check Sample. Since a validated audit material for this method does not exist at this time, it is strongly recommended that a quality control (QC) check sample be used. Chloride solutions of reliably known concentrations are available for purchase from the National Bureau of Standards (SRM 3182). The QC check sample should be analyzed with the calibration standards as a check on the quality of the calibration curve. The QC check sample should be prepared in the sulfuric acid absorbing reagent at a concentration approximately equal to the mid range standard.

4. Procedure

4.1 Sampling.

4.1.1 Preparation of Collection Train. Prepare the sampling train as follows: The first two midget impingers should each be filled with 15 mL of 0.1 N sulfuric acid, and the third and fourth impingers should each be filled with 15 mL of 0.1 N sodium hydroxide. Connect the impingers in series with the knockout impinger first, followed by the two impingers containing the acidified reagent and one impinger containing 0.1 N sodium hydroxide. Place a fresh charge of silica gel, or equivalent, in the drying tube or Mae West impinger.

4.1.2 Leak Check Procedures. Leak check the probe and three-way stopcock prior to inserting the probe into the stack. Connect the stopcock to the outlet of the probe, and connect the sample line to the needle valve. Plug the probe inlet, turn on the sample pump, and pull a vacuum of at least 250 mm Hg (10 in. Hg). Turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds. Place the probe in the stack at the sampling location, and adjust the probe heating system and the stopcock heating system to a temperature sufficient to prevent water condensation. Connect the first impinger to the stopcock, and connect the sample line to the last impinger and the needle valve.

Upon completion of a sampling run, remove the probe from the stack and leak check as described above. If a leak has occurred, the sampling run must be voided. Alternately, the portion of the train behind the probe may be leak checked between multiple runs at the same site as follows: Close the stopcock to the first impinger (see Figure A-1A), and turn on the sample pump. Pull a vacuum of at least 250 mm Hg (10 in. Hg), turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds. Release the vacuum on the impinger train by turning the stopcock to the vent position to permit ambient air to enter (see Figure A-1B). If this procedure is used, the full train leak check described above must be conducted following the final run and all preceding sampling runs voided if a leak has occurred.

4.1.3 Purge Procedure. Immediately prior to sampling, connect the purge line to the stopcock and turn the stopcock to permit the purge pump to purge the probe (see Figure A-1A). Turn on the purge pump, and adjust the purge rate to 2 liters/min. Purge for at least 5 minutes prior to sampling.

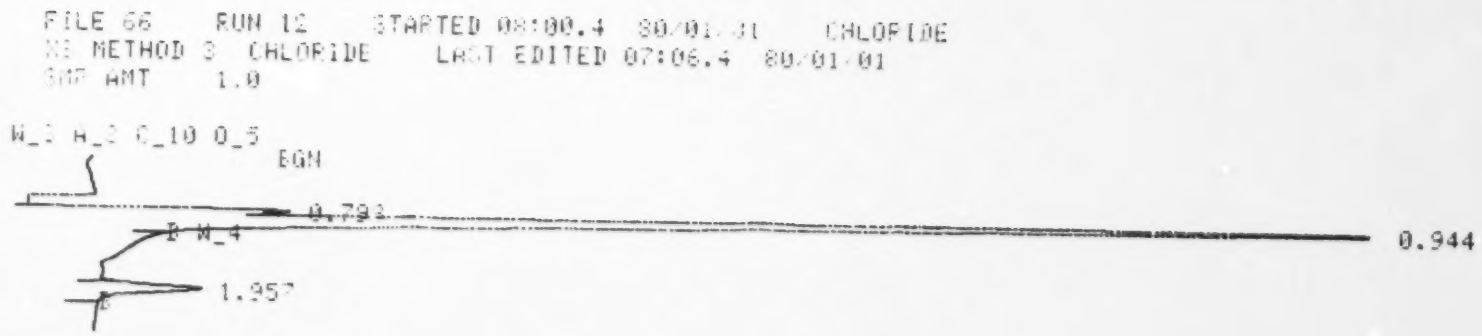
4.1.4 Sample Collection. Turn on sample pump, pull a slight vacuum of approximately 25 mm Hg (1 in. Hg) on the impinger train, and turn the stopcock to permit stack gas to be pulled through the impinger train (see Figure A-1C). Adjust the sampling rate to 2 liters/min, as indicated by the rate meter, and maintain this rate to within 10% during the entire sampling run. Take readings of the dry gas meter, the dry gas meter temperature, rate meter, and vacuum gauge at least once every five minutes during the run. A sampling time of one hour is recommended. Shorter sampling times may introduce a significant negative bias in the HCl concentration.[1] At the conclusion of the sampling run, remove the train from the stack, cool, and perform a leak check as described in Section 4.1.2.

4.2 Sample Recovery. Disconnect the impingers after sampling. Quantitatively transfer the contents of the first three impingers (the knockout impinger and the two acidified water impingers) to a leak-free storage bottle. Add the water rinses of each of these impingers and connecting glassware to the storage bottle. The contents of the impingers and connecting glassware from the second set of impingers (containing the 0.1 N NaOH) can be discarded. The sample bottle should be sealed, shaken to mix, and labeled; the fluid level should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied.

4.3 Sample Preparation for Analysis. Check the liquid level in each sample, and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between the initial and final solution levels, and this value can be used to correct the analytical results. Quantitatively transfer the sample solution to a 100 mL volumetric flask, and dilute the solution to 100 mL with water.

4.4 Sample Analysis. The ion chromatographic conditions will depend on the type of analytical column used and whether suppressed or non-suppressed ion chromatography is used. An example chromatogram from a system using non-suppressed ion chromatography with a 150 mm Hamilton PRP-X100 anion column, a 2 ml/min flow rate of a 4 mM 4-hydroxy benzoate solution adjusted to a pH of 8.6 using 1 N sodium hydroxide, a 50 ul sample loop, and a conductivity detector set on 1.0 uS full scale is shown in Figure A-2. Prior to sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl^- appears in the chromatogram. If Cl^- is present, repeat the load/injection procedure until no Cl^- is present. At this point, the instrument is ready for use.

First, inject the calibration standards covering an appropriate concentration range, starting with the lowest concentration standard. Next, inject, in duplicate, a QC check sample, followed by a water blank and the field samples. Finally, repeat the injection of the calibration standards to allow compensation for any drift in the response of the instrument during analysis of field samples. Measure the Cl^- areas, or heights, of the sample peaks. Use the average response (peak areas or heights) from the duplicate injections to determine the concentrations of field samples using a linear calibration curve calculated from the areas, or heights, arising from injection of standards.



FILE 66 RUN 12 STARTED 08:00.4 80/01/01 CHLORIDE
XS METHOD 3 CHLORIDE LAST EDITED 07:06.4 80/01/01
SMP AMT 1.0

RT	AREA	BC	RT/10	RF	UG/ML	NAME
1.957	46359	0.196	1.000000E+00	46359.0000	CL	

1 MATCHED COMPONENT 7.04% OF TOTAL AREA
2 UNKNOWN PEAKS > UNRET PK 92.96% OF TOTAL AREA
2 PEAKS > AREA REJECT 658312 TOTAL AREA

Figure A-2. Example ion chromatograph.

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4.5 Audit Analysis. There is currently no validated audit sample for this method. Analysis of the QC check sample along with the field samples, as described above, is recommended.

5. Calibration

5.1 Dry Gas Metering System.

5.1.1 Initial Calibration. Before its initial use in the field, first leak check the metering system (sample line, drying tube, vacuum gauge, needle valve, pump, rate meter, and dry gas meter) as follows: plug the inlet end of the sampling line, pull a vacuum of 250 mm (10 in.) Hg, plug off the outlet of the dry gas meter, and turn off the pump. The vacuum should remain stable for 30 seconds. Carefully release the vacuum from the system by slowly removing the plug from the sample line inlet.

Remove the sampling line (and drying tube), and connect the dry gas metering system to a appropriately sized wet test meter (e.g., 1 liter per revolution). Make three independent calibration runs, using at least five revolutions of the dry gas meter per run. Calculate the calibration factor, Y (wet test meter calibration volume divided by the dry gas meter volume, with both volumes adjusted to the same reference temperature and pressure), for each run, and average the results. If any Y value deviates by more than 2 percent from the average, the metering system is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

5.1.2 Post-Test Calibration Check. After each field test series, conduct a calibration check as in Section 5.1.1 above, except for the following variations: (a) the leak check is not to be conducted, (b) three or more revolutions of the dry gas meter may be used, (c) only two independent runs need to be made. If the calibration factor does not deviate by more than 5 percent from the initial calibration factor (determined in Section 5.1.1), then the dry gas meter volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as Section 5.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

5.2 Thermometer. Calibrate against mercury-in-glass thermometers.

5.3 Rate Meter. The rate meter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instructions.

5.4 Barometer. Calibrate against a mercury barometer.

5.5 Calibration Curve for Ion Chromatograph. To prepare calibration standards, dilute given volumes (1.0 mL or greater) of the stock standard solution, with 0.1 $\underline{N}$ H_2SO_4 (Section 3.1.2) to convenient volumes. Prepare at least four standards that are within the linear range of the ion chromatograph, and which cover the expected concentration range of the field samples. Analyze standards as instructed in Section 4.4, beginning with the lowest concentration

standard. Determine the peak areas, or heights, and plot individual values versus Cl^- concentration in ug/mL. Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

6. Calculations

Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

6.1 Sample Volume, Dry Basis, Corrected to Standard Conditions. Calculate as described below:

$$V_{m(std)} = V_m Y \left[\frac{T_{std}}{T_m}\right]\left[\frac{P_{bar}}{P_{std}}\right] = K_1 Y \frac{V_m P_{bar}}{T_m}$$

Where:
K_1 = 0.3858°K/mm Hg for metric units.
= 17.64°R/in. Hg for English units.

6.2 Total ug HCl Per Sample. Calculate as described below:

$$m = (S-B) \times 100 \times 36.46/35.453 = 102.84\ (S-B)$$

Where:
m = Mass of HCl in sample, ug,
S = Analysis of sample, ug Cl^-/mL,
B = Analysis of blank, ug Cl^-/mL,
100 = Volume of filtered and diluted sample, mL,
36.46 = Molecular weight of HCl, ug/ug-mole, and
35.453 = Atomic weight of Cl, ug/ug-mole.

6.3 Concentration of HCl in the Flue Gas. Calculate as described below:

$$C = K \times m/V_{m(std)}$$

Where:
C = Concentration of HCl, dry basis, mg/dscm,
K = 10^{-3} mg/ug,
m = Mass of HCl in sample, ug, and
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm.

7. Bibliography

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3. Entropy Environmentalists Inc., "Laboratory Evaluation of a Sampling and Analysis Method for Hydrogen Chloride Emissions from Stationary Sources: Interim Report," EPA Contract No. 68-02-4442, Research Triangle Park, North Carolina, January 22, 1988.

APPENDIX B.

CALCULATION OF CONTINUOUS EMISSION MONITORING SYSTEM PRECISION

The precision of the continuous emission monitoring system (CEMS) expressed as the standard deviation can be calculated from the precision of the manual HCl method and the bias of the CEMS relative to the manual method as follows:

The precision (or standard deviation), s_m, for the manual method is calculated from the difference, d_i, of the paired trains:

$$s_m = \left[\sum_{i=1}^{n} d_i^2/(2n) \right]^{1/2}$$

where:

n = Number of train pairs.

The i^{th} HCl measurement value of the manual method is:

$$Y_{mi} = A_i + \epsilon_{mi}$$

where:

A_i = True value for HCl concentration, and

ϵ_{mi} = Error term for manual method.

For the CEMS, the i^{th} HCl measurement value is:

$$Y_{ci} = A_i + B + \epsilon_{ci}$$

where:

B = Monitor bias, a constant, and

ϵ_{ci} = Error term for CEMS.

Then, the difference between the monitor value and the manual method value,

$$D_i = Y_{ci} - Y_{mi} = B + \epsilon_{ci} - \epsilon_{mi}.$$

Consequently, the variance of the difference or bias equals the variance for the CEMS plus the variance for the manual method:

$$s_D^2 = s_c^2 + s_m^2$$

And the monitor precision, s_c, can be calculated from the precision of the manual method and the bias of the monitor.